

PATENT COOPERATION TREATY

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Assistant Commissioner for Patents
 United States Patent and Trademark
 Office
 Box PCT
 Washington, D.C.20231
 ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 18 August 2000 (18.08.00)	
International application No. PCT/US99/24013	Applicant's or agent's file reference 98-33-SE PCT
International filing date (day/month/year) 09 November 1999 (09.11.99)	Priority date (day/month/year) 12 November 1998 (12.11.98)
Applicant SANDERSON, Andrew, J. et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:
 09 June 2000 (09.06.00)

☐ in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was
☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b)

PATENT COOPERATION TREATY

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From the INTERNATIONAL BUREAU

NOTIFICATION OF RECEIPT OF
RECORD COPY

(PCT Rule 24.2(a))

To:

COLTON, Kendrew, H.
Pillsbury Madison & Sutro, LLP
1100 New York Avenue, N.W.
Washington, DC 20005
ETATS-UNIS D'AMERIQUE

Date of mailing (day/month/year) 03 May 2000 (03.05.00)	IMPORTANT NOTIFICATION
Applicant's or agent's file reference 98-33-SE PCT	International application No. PCT/US99/24013

The applicant is hereby notified that the International Bureau has received the record copy of the international application as detailed below.

Name(s) of the applicant(s) and State(s) for which they are applicants:

CORDANT TECHNOLOGIES, INC. (for all designated States except US)
SANDERSON, Andrew, J. et al (for US)

International filing date : 09 November 1999 (09.11.99)
Priority date(s) claimed : 12 November 1998 (12.11.98)
Date of receipt of the record copy
by the International Bureau : 27 April 2000 (27.04.00)
List of designated Offices :

AP : GH,GM,KE,LS,MW,SD,SL,SZ,TZ,UG,ZW
EA : AM,AZ,BY,KG,KZ,MD,RU,TJ,TM
EP : AT,BE,CH,CY,DE,DK,ES,FI,FR,GB,GR,IE,IT,LU,MC,NL,PT,SE
OA : BF,BJ,CF,CG,CI,CM,GA,GN,GW,ML,MR,NE,SN,TD,TG
National : AE,AL,AM,AT,AU,AZ,BA,BB,BG,BR,BY,CA,CH,CN,CR,CU,CZ,DE,DK,DM,EE,ES,FI,GB,
GD,GE,GH,GM,HR,HU,ID,IL,IN,IS,JP,KE,KG,KP,KR,KZ,LC,LK,LR,LS,LT,LU,LV,MA,MD,MG,MK,
MN,MW,MX,NO,NZ,PL,PT,RO,RU,SD,SE,SG,SI,SK,SL,TJ,TM,TR,TT,TZ,UA,UG,US,UZ,VN,YU,ZA,
ZW

ATTENTION

The applicant should carefully check the data appearing in this Notification. In case of any discrepancy between these data and the indications in the international application, the applicant should immediately inform the International Bureau.

In addition, the applicant's attention is drawn to the information contained in the Annex, relating to:

- ☒ time limits for entry into the national phase
☐ confirmation of precautionary designations

PATENT COOPERATION TREATY

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COMMUNICATION OF
INTERNATIONAL APPLICATIONS

(PCT Article 20)

From the INTERNATIONAL BUREAU

Assistant Commissioner for Patents
United States Patent and Trademark
Office
Box PCT
Washington, D.C. 20231
ETATS-UNIS D'AMERIQUE

Date of mailing:

04 May 2000 (04.05.00)

in its capacity as designated Office

The International Bureau transmits herewith copies of the international applications having the following international application numbers and international publication numbers:

International application no.:International publication no.:

PCT/US99/24013

PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT**COMMUNICATION IN CASES FOR WHICH
NO OTHER FORM IS APPLICABLE**

To

COLTON, Kendrew, H.
Pillsbury Madison & Sutro, LLP
1100 New York Avenue, N.W.
Washington, DC 20005
ETATS-UNIS D'AMERIQUE

Date of mailing (day month year) 04 May 2000 (04.05.00)	
Applicant's or agent's file reference 98-33-SE PCT	REPLY DUE see paragraph 1 below
International application No. PCT/US99/24013	International filing date (day month year) 09 November 1999 (09.11.99)
Applicant CORDANT TECHNOLOGIES, INC.	

1. ☐ REPLY DUE within _____ months/days from the above date of mailing
- ☐ NO REPLY DUE, however, see below
- ☒ IMPORTANT COMMUNICATION
- ☐ INFORMATION ONLY

2. COMMUNICATION:

The International Bureau regrets to inform the applicant that, due to the receiving Office's (RO/US) late transmittal of the record copy, the above-referenced international application has not been published promptly after the expiration of 18 months from the priority date, as provided in PCT Article 21(2)(a).

International publication will take place on **15 June 2000 (15.06.00)**.

Meanwhile, the International Bureau (WO) will communicate a copy of the international application to each designated Office, in accordance with PCT Article 20.

A copy of this notification has been sent to the receiving Office (RO/US) and to all designated Offices concerned.

International Bureau of WIPO
48, rue de la Confiance
1202 Yverdon, Suisse

Not to be signed

J. Lertao

PC

REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

International Application No.

International Filing Date

Name of receiving Office and "PCT International Application"

Applicant's or agent's file reference
(if desired) (12 characters maximum) 98-33-SE PCT

Box No. I TITLE OF INVENTION METHOD FOR THE SYNTHESIS OF ENERGETIC THERMOPLASTIC ELASTOMERS IN NON-HALOGENATED SOLVENTS	
Box No. II APPLICANT	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.) CORDANT TECHNOLOGIES, INC. 15 West Temple, Suite 1600 Salt Lake City, Utah 84101-1532 United States of America	
<input type="checkbox"/> This person is also inventor.	
Telephone No.	
Facsimile No.	
Teleprinter No.	
State (that is, country) of nationality: US	State (that is, country) of residence: US
This person is applicant for the purposes of: <input type="checkbox"/> all designated States <input checked="" type="checkbox"/> all designated States except the United States of America <input type="checkbox"/> the United States of America only <input type="checkbox"/> the States indicated in the Supplemental Box	
Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.) SANDERSON, Andrew J. 2711 North, Mountain Road North Ogden, Utah 84414 United States of America	
This person is: <input type="checkbox"/> applicant only <input checked="" type="checkbox"/> applicant and inventor <input type="checkbox"/> inventor only (If this check-box is marked, do not fill in below.)	
State (that is, country) of nationality: GB	State (that is, country) of residence: US
This person is applicant for the purposes of: <input type="checkbox"/> all designated States <input type="checkbox"/> all designated States except the United States of America <input checked="" type="checkbox"/> the United States of America only <input type="checkbox"/> the States indicated in the Supplemental Box	
<input checked="" type="checkbox"/> Further applicants and/or (further) inventors are indicated on a continuation sheet.	
Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE	
The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as: <input checked="" type="checkbox"/> agent <input type="checkbox"/> common representative	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.) Washington, D.C. 20005 United States of America	
Telephone No.	
Teleprinter No.	
<input type="checkbox"/> Address for correspondence: (If the address is not the same as the one indicated above, it must be indicated here.)	

Continuation of Box No. III FURTHER APPLICANTS AND/OR (FURTHER) INVENTOR(S)

If none of the following sub-boxes is used, this sheet is not to be included in the request.

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

EDWARDS, Wayne
600S 610 West
Tremonton, Utah 84337
United States of America

This person is:

- ☐ applicant only
☒ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:
US

State (that is, country) of residence:
US

This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

This person is:

- ☐ applicant only
☐ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:

State (that is, country) of residence:

This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

This person is:

- ☐ applicant only
☐ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:

State (that is, country) of residence:

This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

This person is:

- ☐ applicant only
☐ applicant and inventor

State (that is, country) of nationality:

State (that is, country) of residence:

☐ Further applicants and/or further inventors are indicated on an other continuation sheet

The following designations are hereby made under Rule 4.9(a) (mark the applicable check-boxes; at least one must be marked):

Regional Patent

- ☒ **AP ARIPO Patent:** GH Ghana, GM Gambia, KE Kenya, LS Lesotho, MW Malawi, SD Sudan, SL Sierra Leone, SZ Swaziland, UG Uganda, ZW Zimbabwe, and any other State which is a Contracting State of the Harare Protocol and of the PCT
- ☒ **EA Eurasian Patent:** AM Armenia, AZ Azerbaijan, BY Belarus, KG Kyrgyzstan, KZ Kazakhstan, MD Republic of Moldova, RU Russian Federation, TJ Tajikistan, TM Turkmenistan, and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT
- ☒ **EP European Patent:** AT Austria, BE Belgium, CH and LI Switzerland and Liechtenstein, CY Cyprus, DE Germany, DK Denmark, ES Spain, FI Finland, FR France, GB United Kingdom, GR Greece, IE Ireland, IT Italy, LU Luxembourg, MC Monaco, NL Netherlands, PT Portugal, SE Sweden, and any other State which is a Contracting State of the European Patent Convention and of the PCT
- ☒ **OA OAPI Patent:** BF Burkina Faso, BJ Benin, CF Central African Republic, CG Congo, CI Cote d'Ivoire, CM Cameroon, GA Gabon, GN Guinea, GW Guinea-Bissau, ML Mali, MR Mauritania, NE Niger, SN Senegal, TD Chad, TG Togo, and any other State which is a member State of OAPI and a Contracting State of the PCT (if other kind of protection or treatment desired, specify on dotted line)

National Patent (if other kind of protection or treatment desired, specify on dotted line):

- | | |
|--|--|
| <input checked="" type="checkbox"/> AE United Arab Emirates | <input checked="" type="checkbox"/> LR Liberia |
| <input checked="" type="checkbox"/> AL Albania | <input checked="" type="checkbox"/> LS Lesotho |
| <input checked="" type="checkbox"/> AM Armenia | <input checked="" type="checkbox"/> LT Lithuania |
| <input checked="" type="checkbox"/> AT Austria | <input checked="" type="checkbox"/> LU Luxembourg |
| <input checked="" type="checkbox"/> AU Australia | <input checked="" type="checkbox"/> LV Latvia |
| <input checked="" type="checkbox"/> AZ Azerbaijan | <input checked="" type="checkbox"/> MD Republic of Moldova |
| <input checked="" type="checkbox"/> BA Bosnia and Herzegovina | <input checked="" type="checkbox"/> MG Madagascar |
| <input checked="" type="checkbox"/> BB Barbados | <input checked="" type="checkbox"/> MK The former Yugoslav Republic of Macedonia |
| <input checked="" type="checkbox"/> BG Bulgaria | |
| <input checked="" type="checkbox"/> BR Brazil | <input checked="" type="checkbox"/> MN Mongolia |
| <input checked="" type="checkbox"/> BY Belarus | <input checked="" type="checkbox"/> MW Malawi |
| <input checked="" type="checkbox"/> CA Canada | <input checked="" type="checkbox"/> MX Mexico |
| <input checked="" type="checkbox"/> CH and LI Switzerland and Liechtenstein | <input checked="" type="checkbox"/> NO Norway |
| <input checked="" type="checkbox"/> CN China | <input checked="" type="checkbox"/> NZ New Zealand |
| <input checked="" type="checkbox"/> CU Cuba | <input checked="" type="checkbox"/> PL Poland |
| <input checked="" type="checkbox"/> CZ Czech Republic | <input checked="" type="checkbox"/> PT Portugal |
| <input checked="" type="checkbox"/> DE Germany | <input checked="" type="checkbox"/> RO Romania |
| <input checked="" type="checkbox"/> DK Denmark | <input checked="" type="checkbox"/> RU Russian Federation |
| <input checked="" type="checkbox"/> EE Estonia | <input checked="" type="checkbox"/> SD Sudan |
| <input checked="" type="checkbox"/> ES Spain | <input checked="" type="checkbox"/> SE Sweden |
| <input checked="" type="checkbox"/> FI Finland | <input checked="" type="checkbox"/> SG Singapore |
| <input checked="" type="checkbox"/> GB United Kingdom | <input checked="" type="checkbox"/> SI Slovenia |
| <input checked="" type="checkbox"/> GD Grenada | <input checked="" type="checkbox"/> SK Slovakia |
| <input checked="" type="checkbox"/> GE Georgia | <input checked="" type="checkbox"/> SL Sierra Leone |
| <input checked="" type="checkbox"/> GH Ghana | <input checked="" type="checkbox"/> TJ Tajikistan |
| <input checked="" type="checkbox"/> GM Gambia | <input checked="" type="checkbox"/> TM Turkmenistan |
| <input checked="" type="checkbox"/> HR Croatia | <input checked="" type="checkbox"/> TR Turkey |
| <input checked="" type="checkbox"/> HU Hungary | <input checked="" type="checkbox"/> TT Trinidad and Tobago |
| <input checked="" type="checkbox"/> ID Indonesia | <input checked="" type="checkbox"/> UA Ukraine |
| <input checked="" type="checkbox"/> IL Israel | <input checked="" type="checkbox"/> UG Uganda |
| <input checked="" type="checkbox"/> IN India | <input checked="" type="checkbox"/> US United States of America |
| <input checked="" type="checkbox"/> IS Iceland | |
| <input checked="" type="checkbox"/> JP Japan | <input checked="" type="checkbox"/> UZ Uzbekistan |
| <input checked="" type="checkbox"/> KE Kenya | <input checked="" type="checkbox"/> VN Viet Nam |
| <input checked="" type="checkbox"/> KG Kyrgyzstan | <input checked="" type="checkbox"/> YU Yugoslavia |
| <input checked="" type="checkbox"/> KP Democratic People's Republic of Korea | <input checked="" type="checkbox"/> ZA South Africa |
| <input checked="" type="checkbox"/> EP | <input checked="" type="checkbox"/> ZW Zimbabwe |

Precautionary Designation Statement: In addition to the designation made above, the applicant also make (under Rule 4.9(b)) all other designations which would be permitted under the PCT except any designations indicated in the Supplemental Box as being excluded from the scope of this statement. The applicant declare that those additional designations are subject to confirmation and

Supplemental Box

If the Supplemental Box is not used, this sheet need not be included in the request.

1. If, in any of the Boxes, the space is insufficient to furnish all the information: in such case, write "Continuation of Box No. ..." [indicate the number of the Box] and furnish the information in the same manner as required according to the captions of the Box in which the space was insufficient, in particular:

- (i) if more than two persons are involved as applicants and/or inventors and no "continuation sheet" is available: in such case, write "Continuation of Box No. III" and indicate for each additional person the same type of information as required in Box No. III. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below;
- (ii) if, in Box No. II or in any of the sub-boxes of Box No. III, the indication "the States indicated in the Supplemental Box" is checked: in such case, write "Continuation of Box No. II" or "Continuation of Box No. III" or "Continuation of Boxes No. II and No. III" (as the case may be), indicate the name of the applicant(s) involved and, next to (each) such name, the State(s) (and/or, where applicable, ARIPO, Eurasian, European or OAPI patent) for the purposes of which the named person is applicant;
- (iii) if, in Box No. II or in any of the sub-boxes of Box No. III, the inventor or the inventor/applicant is not inventor for the purposes of all designated States or for the purposes of the United States of America: in such case, write "Continuation of Box No. II" or "Continuation of Box No. III" or "Continuation of Boxes No. II and No. III" (as the case may be), indicate the name of the inventor(s) and, next to (each) name, the State(s) (and/or, where applicable, ARIPO, Eurasian, European or OAPI patent) for the purposes of which the named person is inventor;
- (iv) if, in addition to the agent(s) indicated in Box IV, there are further agents: in such case, write "Continuation of Box No. IV" and indicate for each further agent the same type of information as required in Box No. IV;
- (v) if, in Box No. V, the name of any State (or OAPI) is accompanied by the indication "patent of addition," or "certificate of addition," or if, in Box No. V, the name of the United States of America is accompanied by an indication "continuation" or "continuation-in-part": in such case, write "Continuation of Box No. V" and the name of each State involved (or OAPI), and after the name of each such State (or OAPI), the number of the parent title or parent application and the date of grant of the parent title or filing of the parent application;
- (vi) if, in Box No. VI, there are more than three earlier applications whose priority is claimed: in such case, write "Continuation of Box No. VI" and indicate for each additional earlier application the same type of information as required in Box No. VI.
- (vii) if, in Box No. VI, the earlier application is an ARIPO application: in such case, write "Continuation of Box No. VI", specify the number of the item corresponding to that earlier application and indicate at least one country party to the Paris Convention for the Protection of Industrial Property for which that earlier application was filed.

2. If, with regard to the precautionary designation statement contained in Box No. V, the applicant wishes to exclude any State(s) from the scope of that statement: in such case, write "Designation(s) excluded from precautionary designation statement" and indicate the name or two-letter code of each State so excluded.

3. If the applicant claims, in respect of any designated Office, the benefits of provisions of the national law concerning non-prejudicial disclosures or exceptions to lack of novelty: in such case, write "Statement concerning non-prejudicial disclosures or exceptions to lack of novelty" and furnish that statement below.

Box No. IV. Agent or Common Representative: (continued)

KOKULIS, Paul N.	BIRD, Donald J.	EDGEELL, G. Paul
LIPPITT, Raymond F.	ECCLESTON, Lynn E.	JAKOPIN, David A.
KNIGHT, G. Lloyd	GOWDEY, Peter W.	PAULSON, Mark G.
LOVE, Carl G.	LAZAR, Dale S.	KLIMA, Timothy J.
MARTIN, Edgar H.	PERRY, Glenn J.	McQUADE, Paul F.
	MORDOUCH, Ruth N.	DZWONCZYK, Michael R.
JOYCE, Kevin E.	WHITE, Paul E., Jr.	SIRILLA, George M.
WISE, Roger R.	BENGTSOON, W. Patrick	BARUFFA, Jack s.
ZAITLEN, Richard H.	SMYRSKI, Steven W.	KIRKPATRICK, Anita M.
HESS, Adam R.	GLAZIER, Stephen C.	
FINFELSTEIN, Jay M.	NAGY, Paul G.	

All attorneys are partners of the firm of PILLSBURY MADISON & SUTRO, LLP. The address, telephone number, and

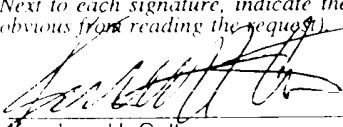
Box No. VI PRIORITY CLAIM		<input type="checkbox"/> Further priority claims are indicated in the Supplemental Box.		
Filing date of earlier application (day/month/year)	Number of earlier application	Where earlier application is:		
		national application: country	regional application:* regional Office	international application: receiving Office
item (1) 12/November/1998 (12/11/98)	60/108,455	US		
item (2)				
item (3)				

☒ The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) (only if the earlier application was filed with the Office which for the purposes of the present international application is the receiving Office) identified above as item(s): (1)

* Where the earlier application is an ARIPO application, it is mandatory to indicate in the Supplemental Box at least one country party to the Paris Convention for the Protection of Industrial Property for which that earlier application was filed (Rule 4.10(b)(ii)). See Supplemental Box.

Box No. VII INTERNATIONAL SEARCHING AUTHORITY	
Choice of International Searching Authority (ISA) (if two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used):	Request to use results of earlier search; reference to that search (if an earlier search has been carried out by or requested from the International Searching Authority): Date (day/month/year) Number Country (or regional Office)
ISA/EP	

Box No. VIII CHECK LIST: LANGUAGE OF FILING	
This international application contains the following number of sheets : request : 5 description (excluding sequence listing part) : 27 claims : 6 abstract : 1 drawings : 2 sequence listing part of description : Total number of sheets : 41	This international application is accompanied by the item(s) marked below: 1. <input checked="" type="checkbox"/> fee calculation sheet 2. <input type="checkbox"/> separate signed power of attorney 3. <input type="checkbox"/> copy of general power of attorney; reference number, if any: 4. <input type="checkbox"/> statement explaining lack of signature 5. <input type="checkbox"/> priority document(s) identified in Box No. VI as item(s): 6. <input type="checkbox"/> translation of international application into (language): 7. <input type="checkbox"/> separate indications concerning deposited microorganism or other biological material 8. <input type="checkbox"/> nucleotide and/or amino acid sequence listing in computer readable form 9. <input checked="" type="checkbox"/> other (specify): Transmittal letter & Postcard
Figure of the drawings which should accompany the abstract:	Language of filing of the international application: English

Box No. IX SIGNATURE OF APPLICANT OR AGENT	
Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request).  Andrew H. Colton	

For receiving Office use only	
1. Date of actual receipt of the purported international application: 01/01/2000	2. Drawings: <input type="checkbox"/> enclosed
3. International Searching Authority (if two or more are competent): ISA/	4. <input type="checkbox"/> Transmittal of search copy delayed until search fee is paid

5. International Searching Authority (if two or more are competent): ISA/

PCT

FEE CALCULATION SHEET

Annex to the Request

For receiving Office use only

International application No.

Applicant's or agent's
file reference

98-33-SE PCT

Date stamp of the receiving Office

Applicant

CORDANT TECHNOLOGIES, INC.

CALCULATION OF PRESCRIBED FEES

1. TRANSMITTAL FEE 240.00 T

2. SEARCH FEE 1,002.00 S

International search to be carried out by EP

(If two or more International Searching Authorities are competent in relation to the international application, indicate the name of the Authority which is chosen to carry out the international search.)

3. INTERNATIONAL FEE

Basic Fee

The international application contains 41 sheets.

first 30 sheets 455.00 b₁

11	x	\$10.00	=	110.00	b ₂
remaining sheets		additional amount			

Add amounts entered at b₁ and b₂ and enter total at B 565.00 B

Designation Fees

The international application contains ALL designations.

10	x	105.00	=	1,050.00	D
number of designation fees payable (maximum 10)		amount of designation fee			

Add amounts entered at B and D and enter total at I 1,615.00 I

(Applicants from certain States are entitled to a reduction of 75% of the international fee. Where the applicant is (or all applicants are) so entitled, the total to be entered at I is 25% of the sum of the amounts entered at B and D.)

4. FEE FOR PRIORITY DOCUMENT (if applicable) 15.00 P

5. TOTAL FEES PAYABLE

Add amounts entered at T, S, I and P, and enter total in the TOTAL box

2,872.00

TOTAL

☐ The designation fees are not paid at this time.

MODE OF PAYMENT

☒ authorization to charge
deposit account (see below)☐ bank draft☐ coupons☒ cheque☐ cash☐ other (specify):☐ postal money order☐ revenue stamps☒ I hereby authorize the receiving Office to debit my deposit account for the total fees indicated above to my deposit account.☐ I hereby authorize to charge the fee for preparation and transmittal of the priority document to the International Bureau.

03-3975

05 November 1999

Deposit Account Number

Date (day month year)

Signature Kendrew H. Colton

IPEA/ EP

PCT

CHAPTER II

DEMAND

under Article 31 of the Patent Cooperation Treaty:
The undersigned requests that the international application specified below be the subject of international preliminary examination according to the Patent Cooperation Treaty and hereby elects all eligible States (except where otherwise indicated).

For International Preliminary Examining Authority use only													
Identification of IPEA	Date of receipt of DEMAND												
<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td colspan="2" style="padding: 5px;">Box No. I IDENTIFICATION OF THE INTERNATIONAL APPLICATION</td> <td style="padding: 5px;">Applicant's or agent's file reference 98-33-SE PCT</td> </tr> <tr> <td style="width: 33%; padding: 5px;">International application No. PCT/US99/24013</td> <td style="width: 33%; padding: 5px;">International filing date (day/month/year) 09 November 1999 (09.11.99)</td> <td style="width: 34%; padding: 5px;">(Earliest) Priority date (day/month/year) 12 November 1998 (12.11.98)</td> </tr> <tr> <td colspan="3" style="padding: 5px;">Title of invention METHOD FOR THE SYNTHESIS OF ENERGETIC THERMOPLASTIC ELASTOMERS IN NON-HALOGENATED SOLVENTS</td> </tr> </table>		Box No. I IDENTIFICATION OF THE INTERNATIONAL APPLICATION		Applicant's or agent's file reference 98-33-SE PCT	International application No. PCT/US99/24013	International filing date (day/month/year) 09 November 1999 (09.11.99)	(Earliest) Priority date (day/month/year) 12 November 1998 (12.11.98)	Title of invention METHOD FOR THE SYNTHESIS OF ENERGETIC THERMOPLASTIC ELASTOMERS IN NON-HALOGENATED SOLVENTS					
Box No. I IDENTIFICATION OF THE INTERNATIONAL APPLICATION		Applicant's or agent's file reference 98-33-SE PCT											
International application No. PCT/US99/24013	International filing date (day/month/year) 09 November 1999 (09.11.99)	(Earliest) Priority date (day/month/year) 12 November 1998 (12.11.98)											
Title of invention METHOD FOR THE SYNTHESIS OF ENERGETIC THERMOPLASTIC ELASTOMERS IN NON-HALOGENATED SOLVENTS													
Box No. II APPLICANT(S)													
<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 60%; padding: 5px;"> Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.) CORDANT TECHNOLOGIES, INC. 15 West Temple, Suite 1600 Salt Lake City, Utah 84101-1532 United States of America </td> <td style="width: 40%; padding: 5px;"> Telephone No.: Facsimile No.: Teleprinter No.: </td> </tr> <tr> <td style="padding: 5px;"> State (that is, country) of nationality: US </td> <td style="padding: 5px;"> State (that is, country) of residence: US </td> </tr> <tr> <td colspan="2" style="padding: 5px;"> Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.) SANDERSON, Andrew J. 2711 North, Mountain Road North Ogden, Utah 84414 United States of America </td> </tr> <tr> <td style="padding: 5px;"> State (that is, country) of nationality: US </td> <td style="padding: 5px;"> State (that is, country) of residence: US </td> </tr> <tr> <td colspan="2" style="padding: 5px;"> Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.) EDWARDS, Wayne 600S 610 West Tremonton, Utah 84327 </td> </tr> <tr> <td style="padding: 5px;"> State (that is, country) of nationality: US </td> <td style="padding: 5px;"> State (that is, country) of residence: US </td> </tr> </table>		Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.) CORDANT TECHNOLOGIES, INC. 15 West Temple, Suite 1600 Salt Lake City, Utah 84101-1532 United States of America	Telephone No.: Facsimile No.: Teleprinter No.:	State (that is, country) of nationality: US	State (that is, country) of residence: US	Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.) SANDERSON, Andrew J. 2711 North, Mountain Road North Ogden, Utah 84414 United States of America		State (that is, country) of nationality: US	State (that is, country) of residence: US	Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.) EDWARDS, Wayne 600S 610 West Tremonton, Utah 84327		State (that is, country) of nationality: US	State (that is, country) of residence: US
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.) CORDANT TECHNOLOGIES, INC. 15 West Temple, Suite 1600 Salt Lake City, Utah 84101-1532 United States of America	Telephone No.: Facsimile No.: Teleprinter No.:												
State (that is, country) of nationality: US	State (that is, country) of residence: US												
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.) SANDERSON, Andrew J. 2711 North, Mountain Road North Ogden, Utah 84414 United States of America													
State (that is, country) of nationality: US	State (that is, country) of residence: US												
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.) EDWARDS, Wayne 600S 610 West Tremonton, Utah 84327													
State (that is, country) of nationality: US	State (that is, country) of residence: US												
<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; padding: 5px;"> State (that is, country) of nationality: US </td> <td style="width: 50%; padding: 5px;"> State (that is, country) of residence: US </td> </tr> <tr> <td colspan="2" style="padding: 5px;"> <input type="checkbox"/> </td> </tr> </table>		State (that is, country) of nationality: US	State (that is, country) of residence: US	<input type="checkbox"/>									
State (that is, country) of nationality: US	State (that is, country) of residence: US												
<input type="checkbox"/>													

Box No. III AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE

The following person is ☒ agent ☐ common representative
 and ☒ has been appointed earlier and represents the applicant(s) also for international preliminary examination.
☐ is hereby appointed and any earlier appointment of (an) agent(s) /common representative is hereby revoked.
☐ is hereby appointed, specifically for the procedure before the International Preliminary Examining Authority, in addition to the agent(s)/common representative appointed earlier.

Name and address: *(Family name followed by given name; for a legal entity, full official designation.)*
The address must include postal code and name of country.)

COLTON, Kendrew H.
 PILLSBURY MADISON & SUTRO, LLP
 1100 New York Avenue, NW
 Washington, DC 20005
 United States of America

Telephone No.:
202 861-3000

Facsimile No.:
202 822-0944

Teleprinter No.:

☐ Address for correspondence: Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.

Box No. IV BASIS FOR INTERNATIONAL PRELIMINARY EXAMINATION**Statement concerning amendments:***

1. The applicant wishes the international preliminary examination to start on the basis of:

- ☒ the international application as originally filed
 the description ☐ as originally filed
☒ as amended under Article 34
 the claims ☒ as originally filed
☐ as amended under Article 19 (together with any accompanying statement)
☐ as amended under Article 34
 the drawings ☒ as originally filed
☐ as amended under Article 34

2. ☐ The applicant wishes any amendment to the claims under Article 19 to be considered as reversed.

3. ☐ The applicant wishes the start of the international preliminary examination to be postponed until the expiration of 20 months from the priority date unless the International Preliminary Examining Authority receives a copy of any amendments made under Article 19 or a notice from the applicant that he does not wish to make such amendments (Rule 69.1(d)). *(This check-box may be marked only where the time limit under Article 19 has not yet expired.)*

* Where no check-box is marked, international preliminary examination will start on the basis of the international application as originally filed or, where a copy of amendments to the claims under Article 19 and/or amendments of the international application under Article 34 are received by the International Preliminary Examining Authority before it has begun to draw up a written opinion or the international preliminary examination report, as so amended.

Language for the purposes of international preliminary examination: English

- ☒ which is the language in which the international application was filed.
☐ which is the language of a translation furnished for the purposes of international search.

Box No. V ELECTION OF STATES

The applicant hereby elects all eligible States *(that is, all States which have been designated and which are bound by Chapter II of the PCT)*

or, to file the following States which the applicant does not elect:

Box No. VI CHECK LIST

The demand is accompanied by the following elements, in the language referred to in Box No. IV, for the purposes of international preliminary examination:

- | | | |
|--|---|----------------|
| 1. translation of international application | : | _____ sheets |
| 2. amendments under Article 34 | : | 2 _____ sheets |
| 3. copy (or, where required, translation) of amendments under Article 19 | : | _____ sheets |
| 4. copy (or, where required, translation) of statement under Article 19 | : | _____ sheets |
| 5. letter | : | 1 _____ sheets |
| 6. other (<i>specify</i>) | : | _____ sheets |

For International Preliminary Examining Authority use only

received not received

<input type="checkbox"/>	<input type="checkbox"/>
<input type="checkbox"/>	<input type="checkbox"/>
<input type="checkbox"/>	<input type="checkbox"/>
<input type="checkbox"/>	<input type="checkbox"/>
<input type="checkbox"/>	<input type="checkbox"/>
<input type="checkbox"/>	<input type="checkbox"/>

The demand is also accompanied by the item(s) marked below:

- | | |
|--|---|
| 1. <input checked="" type="checkbox"/> fee calculation sheet | 4. <input type="checkbox"/> statement explaining lack of signature |
| 2. <input type="checkbox"/> separate signed power of attorney | 5. <input type="checkbox"/> nucleotide and or amino acid sequence listing in computer readable form |
| 3. <input type="checkbox"/> copy of general power of attorney; reference number, if any: | 6. <input checked="" type="checkbox"/> other (<i>specify</i>): Receipt |

Box No. VII SIGNATURE OF APPLICANT, AGENT OR COMMON REPRESENTATIVE

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the demand).



Kendrew H. Colton

For International Preliminary Examining Authority use only

1. Date of actual receipt of DEMAND:

2. Adjusted date of receipt of demand due to CORRECTIONS under Rule 60.1(b):

3. ☐ The date of receipt of the demand is AFTER the expiration of 19 months from the priority date and item 4 or 5, below, does not apply.

☐ The applicant has been informed accordingly.

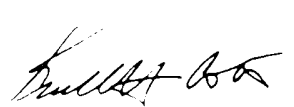
☐ Although the date of receipt of the demand is after the expiry date, the demand is nevertheless timely, since the delay in filing was EXCUSED pursuant to Rule 82

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FEE CALCULATION SHEET

Annex to the Demand for international preliminary examination

International application No. PCT/US99/24013	For International Preliminary Examining Authority use only	
Applicant's or agent's file reference 98-33-SE PCT	Date stamp of the IPEA	
Applicant CORDANT TECHNOLOGIES, INC.		
Calculation of prescribed fees		
1. Preliminary examination fee	2,998.29	<div style="border: 1px solid black; width: 20px; height: 20px; display: flex; align-items: center; justify-content: center;">P</div>
2. Handling fee <i>(Applicants from certain States are entitled to a reduction of 75% of the handling fee. Where the applicant is (or all applicants are) so entitled, the amount to be entered at H is 25% of the handling fee.)</i>	287.51	<div style="border: 1px solid black; width: 20px; height: 20px; display: flex; align-items: center; justify-content: center;">H</div>
3. Total of prescribed fees Add the amounts entered at P and H and enter total in the TOTAL box	<div style="border: 1px solid black; padding: 5px; width: 100px;"> 3,285.80 </div>	
	<div style="border: 1px solid black; padding: 5px; width: 100px;"> TOTAL </div>	
Mode of Payment		
<input type="checkbox"/> authorization to charge deposit account with the IPEA (see below)	<input type="checkbox"/> cash	
<input type="checkbox"/> cheque	<input type="checkbox"/> revenue stamps	
<input type="checkbox"/> postal money order	<input type="checkbox"/> coupons	
<input checked="" type="checkbox"/> bank draft	<input type="checkbox"/> other (specify):	
Deposit Account Authorization <i>(this mode of payment may not be available at all IPEAs)</i>		
The IPEA <input type="checkbox"/> is hereby authorized to charge the total fee in United States dollars to the account of the applicant.		
<div style="display: flex; justify-content: space-between; align-items: flex-end;"> <div style="text-align: center;"> 09 June 2000 <small>Date of payment</small> </div> <div style="text-align: center;">  <small>Signature</small> </div> </div>		

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference 98-33-SE PCT	FOR FURTHER ACTION see Notification of Transmittal of International Search Report (Form PCT ISA/220) as well as, where applicable, item 5 below.	
International application No. PCT/US 99/ 24013	International filing date (day, month, year) 09/11/1999	(Earliest) Priority Date (day, month, year) 12/11/1998
Applicant CORDANT TECHNOLOGIES, INC. et al.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 2 sheets.
☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.
- ☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).
- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing:
- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

2 ☐ **Certain claims were found unsearchable** (See Box I).

3 ☐ **Unity of invention is lacking** (see Box II)

4 With regard to the title.

- ☐ the text is approved as submitted by the applicant
- ☒ the text has been established by this Authority to read as follows:

METHOD FOR THE SYNTHESIS OF THERMOPLASTIC ELASTOMERS IN NON-HALOGENATED SOLVENTS

5 With regard to the abstract.

- ☐ the drawings have been established by this Authority as suggested by the applicant
- ☐ because the applicant failed to suggest a figure
- ☐ None of the figures

INTERNATIONAL SEARCH REPORT

International Application No.

P 99/24013

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08G18/48 C08G18/08 C08G18/76

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G C06B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 2 307 688 A (THIOKOL) 4 June 1997 (1997-06-04) claims; examples ---	1-3, 12-21, 30-33
A	US 5 210 153 A (MANSE ET AL) 11 May 1993 (1993-05-11) column 6, line 27 - line 36; claims 1,7; examples ---	1-3, 15-21, 30-33
A	US 4 806 613 A (WARDLE) 21 February 1989 (1989-02-21) cited in the application claims; examples -----	1-3, 12-21, 30-33



Further documents are listed in the continuation of box C



Patent family members are listed in annex

Special categories of cited documents:

A document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

4 September 2000

11.09.2000

Name and address of the ISA

European Patent Office (EPO) Patent Department

Strassburger Allee 1

D-60486 Frankfurt am Main

Authorized Officer

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

P/S 99/24013

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
GB 2307688	A	04-06-1997	NONE	
US 5210153	A	11-05-1993	NONE	
US 4806613	A	21-02-1989	CA 1318052 A	18-05-1993
			DE 68928734 D	20-08-1998
			DE 68928734 T	21-01-1999
			EP 0335499 A	04-10-1989
			JP 2014216 A	18-01-1990
			JP 2705821 B	28-01-1998

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RECEIVED

REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

PCT/US 99/24013	
International Application No.	(09.11.99)
International Filing Date	09 NOV 1999
PCT INTERNATIONAL APPLICATION PCT/US	
Name of Receiving Office: "PCT International Application"	
Applicant's or agent's file reference (if desired) (12 characters maximum)	98-33-SE PCT

Box No. I TITLE OF INVENTION METHOD FOR THE SYNTHESIS OF ENERGETIC THERMOPLASTIC ELASTOMERS IN NON-HALOGENATED SOLVENTS	
Box No. II APPLICANT	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.) CORDANT TECHNOLOGIES, INC. 15 West Temple, Suite 1600 Salt Lake City, Utah 84101-1532 United States of America	<input type="checkbox"/> This person is also inventor. Telephone No. Facsimile No. Teleprinter No.
State (that is, country) of nationality: US	State (that is, country) of residence: US
This person is applicant for the purposes of: <input type="checkbox"/> all designated States <input checked="" type="checkbox"/> all designated States except the United States of America <input type="checkbox"/> the United States of America only <input type="checkbox"/> the States indicated in the Supplemental Box	
Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.) SANDERSON, Andrew J. 2711 North, Mountain Road North Ogden, Utah 84414 United States of America	This person is: <input type="checkbox"/> applicant only <input checked="" type="checkbox"/> applicant and inventor <input type="checkbox"/> inventor only (If this check-box is marked, do not fill in below.)
State (that is, country) of nationality: GB	State (that is, country) of residence: US
This person is applicant for the purposes of: <input type="checkbox"/> all designated States <input type="checkbox"/> all designated States except the United States of America <input checked="" type="checkbox"/> the United States of America only <input type="checkbox"/> the States indicated in the Supplemental Box	
<input checked="" type="checkbox"/> Further applicants and/or (further) inventors are indicated on a continuation sheet.	
Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE	
The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as: <input checked="" type="checkbox"/> agent <input type="checkbox"/> common representative	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.) 202 861 3000	

Washington, D.C. 20005
United States of America

Teleprinter No.



Address for correspondence: Mailing address

Continuation of Box No. III FURTHER APPLICANTS AND/OR (FURTHER) INVENTOR(S)

If none of the following sub-boxes is used, this sheet is not to be included in the request.

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

EDWARDS, Wayne
600S 610 West
Tremonton, Utah 84337
United States of America

This person is:

- ☐ applicant only
☒ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:
US

State (that is, country) of residence:
US

This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

This person is:

- ☐ applicant only
☐ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:

State (that is, country) of residence:

This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

This person is:

- ☐ applicant only
☐ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:

State (that is, country) of residence:

This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

This person is:

- ☐ applicant only
☐ applicant and inventor
☐

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

State (that is, country) of residence:

This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

☐ I am not an applicant or inventor.

Box No.V DESIGNATION OF STATES

The following designations are hereby made under Rule 4.9(a) (mark the applicable check-boxes; at least one must be marked):

Regional Patent

- ☒ **AP ARIPO Patent:** GH Ghana, GM Gambia, KE Kenya, LS Lesotho, MW Malawi, SD Sudan, SL Sierra Leone, SZ Swaziland, UG Uganda, ZW Zimbabwe, and any other State which is a Contracting State of the Harare Protocol and of the PCT
- ☒ **EA Eurasian Patent:** AM Armenia, AZ Azerbaijan, BY Belarus, KG Kyrgyzstan, KZ Kazakhstan, MD Republic of Moldova, RU Russian Federation, TJ Tajikistan, TM Turkmenistan, and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT
- ☒ **EP European Patent:** AT Austria, BE Belgium, CH and LI Switzerland and Liechtenstein, CY Cyprus, DE Germany, DK Denmark, ES Spain, FI Finland, FR France, GB United Kingdom, GR Greece, IE Ireland, IT Italy, LU Luxembourg, MC Monaco, NL Netherlands, PT Portugal, SE Sweden, and any other State which is a Contracting State of the European Patent Convention and of the PCT
- ☒ **OA OAPI Patent:** BF Burkina Faso, BJ Benin, CF Central African Republic, CG Congo, CI Cote d'Ivoire, CM Cameroon, GA Gabon, GN Guinea, GW Guinea-Bissau, ML Mali, MR Mauritania, NE Niger, SN Senegal, TD Chad, TG Togo, and any other State which is a member State of OAPI and a Contracting State of the PCT (if other kind of protection or treatment desired, specify on dotted line)

National Patent (if other kind of protection or treatment desired, specify on dotted line):

- | | |
|--|--|
| <input checked="" type="checkbox"/> AE United Arab Emirates | <input checked="" type="checkbox"/> LR Liberia |
| <input checked="" type="checkbox"/> AL Albania | <input checked="" type="checkbox"/> LS Lesotho |
| <input checked="" type="checkbox"/> AM Armenia | <input checked="" type="checkbox"/> LT Lithuania |
| <input checked="" type="checkbox"/> AT Austria | <input checked="" type="checkbox"/> LU Luxembourg |
| <input checked="" type="checkbox"/> AU Australia | <input checked="" type="checkbox"/> LV Latvia |
| <input checked="" type="checkbox"/> AZ Azerbaijan | <input checked="" type="checkbox"/> MD Republic of Moldova |
| <input checked="" type="checkbox"/> BA Bosnia and Herzegovina | <input checked="" type="checkbox"/> MG Madagascar |
| <input checked="" type="checkbox"/> BB Barbados | <input checked="" type="checkbox"/> MK The former Yugoslav Republic of Macedonia |
| <input checked="" type="checkbox"/> BG Bulgaria | |
| <input checked="" type="checkbox"/> BR Brazil | <input checked="" type="checkbox"/> MN Mongolia |
| <input checked="" type="checkbox"/> BY Belarus | <input checked="" type="checkbox"/> MW Malawi |
| <input checked="" type="checkbox"/> CA Canada | <input checked="" type="checkbox"/> MX Mexico |
| <input checked="" type="checkbox"/> CH and LI Switzerland and Liechtenstein | <input checked="" type="checkbox"/> NO Norway |
| <input checked="" type="checkbox"/> CN China | <input checked="" type="checkbox"/> NZ New Zealand |
| <input checked="" type="checkbox"/> CU Cuba | <input checked="" type="checkbox"/> PL Poland |
| <input checked="" type="checkbox"/> CZ Czech Republic | <input checked="" type="checkbox"/> PT Portugal |
| <input checked="" type="checkbox"/> DE Germany | <input checked="" type="checkbox"/> RO Romania |
| <input checked="" type="checkbox"/> DK Denmark | <input checked="" type="checkbox"/> RU Russian Federation |
| <input checked="" type="checkbox"/> EE Estonia | <input checked="" type="checkbox"/> SD Sudan |
| <input checked="" type="checkbox"/> ES Spain | <input checked="" type="checkbox"/> SE Sweden |
| <input checked="" type="checkbox"/> FI Finland | <input checked="" type="checkbox"/> SG Singapore |
| <input checked="" type="checkbox"/> GB United Kingdom | <input checked="" type="checkbox"/> SI Slovenia |
| <input checked="" type="checkbox"/> GD Grenada | <input checked="" type="checkbox"/> SK Slovakia |
| <input checked="" type="checkbox"/> GE Georgia | <input checked="" type="checkbox"/> SL Sierra Leone |
| <input checked="" type="checkbox"/> GH Ghana | <input checked="" type="checkbox"/> TJ Tajikistan |
| <input checked="" type="checkbox"/> GM Gambia | <input checked="" type="checkbox"/> TM Turkmenistan |
| <input checked="" type="checkbox"/> HR Croatia | <input checked="" type="checkbox"/> TR Turkey |
| <input checked="" type="checkbox"/> HU Hungary | <input checked="" type="checkbox"/> TT Trinidad and Tobago |
| <input checked="" type="checkbox"/> ID Indonesia | <input checked="" type="checkbox"/> UA Ukraine |
| <input checked="" type="checkbox"/> IL Israel | <input checked="" type="checkbox"/> UG Uganda |
| <input checked="" type="checkbox"/> IN India | <input checked="" type="checkbox"/> US United States of America |
| <input checked="" type="checkbox"/> IS Iceland | |
| <input checked="" type="checkbox"/> JP Japan | <input checked="" type="checkbox"/> UZ Uzbekistan |
| <input checked="" type="checkbox"/> KE Kenya | <input checked="" type="checkbox"/> VN Viet Nam |
| <input checked="" type="checkbox"/> KG Kyrgyzstan | <input checked="" type="checkbox"/> YU Yugoslavia |
| <input checked="" type="checkbox"/> KP Democratic People's Republic of Korea | <input checked="" type="checkbox"/> ZA South Africa |
| | <input checked="" type="checkbox"/> ZW Zimbabwe |
| <input checked="" type="checkbox"/> KR Republic of Korea | |

Check-boxes reserved for designating States which have become

Precautionary Designation Statement

I declare that, in addition to the designations marked above, the applicant also makes and intends to make other designations which would be permitted under the PCT except any designation(s) indicated in the Supplemental Box as being excluded from the scope of this statement. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed must be the exception of 15 months from the priority date of the basic patent.

Supplemental Box *If the Supplemental Box is not used, this sheet need not be included in the request.*

1. If, in any of the Boxes, the space is insufficient to furnish all the information: in such case, write "Continuation of Box No. ..." [indicate the number of the Box] and furnish the information in the same manner as required according to the captions of the Box in which the space was insufficient, in particular:

- (i) if more than two persons are involved as applicants and/or inventors and no "continuation sheet" is available: in such case, write "Continuation of Box No. III" and indicate for each additional person the same type of information as required in Box No. III. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below;
- (ii) if, in Box No. II or in any of the sub-boxes of Box No. III, the indication "the States indicated in the Supplemental Box" is checked: in such case, write "Continuation of Box No. II" or "Continuation of Box No. III" or "Continuation of Boxes No. II and No. III" (as the case may be), indicate the name of the applicant(s) involved and, next to (each) such name, the State(s) (and/or, where applicable, ARIPO, Eurasian, European or OAPI patent) for the purposes of which the named person is applicant;
- (iii) if, in Box No. II or in any of the sub-boxes of Box No. III, the inventor or the inventor/applicant is not inventor for the purposes of all designated States or for the purposes of the United States of America: in such case, write "Continuation of Box No. II" or "Continuation of Box No. III" or "Continuation of Boxes No. II and No. III" (as the case may be), indicate the name of the inventor(s) and, next to (each) name, the State(s) (and/or, where applicable, ARIPO, Eurasian, European or OAPI patent) for the purposes of which the named person is inventor;
- (iv) if, in addition to the agent(s) indicated in Box IV, there are further agents: in such case, write "Continuation of Box No. IV" and indicate for each further agent the same type of information as required in Box No. IV;
- (v) if, in Box No. V, the name of any State (or OAPI) is accompanied by the indication "patent of addition," or "certificate of addition," or if, in Box No. V., the name of the United States of America is accompanied by an indication "continuation" or "continuation-in-part": in such case, write "Continuation of Box No. V" and the name of each State involved (or OAPI), and after the name of each such State (or OAPI), the number of the parent title or parent application and the date of grant of the parent title or filing of the parent application;
- (vi) if, in Box No. VI, there are more than three earlier applications whose priority is claimed: in such case, write "Continuation of Box No. VI" and indicate for each additional earlier application the same type of information as required in Box No. VI;
- (vii) if, in Box No. VI, the earlier application is an ARIPO application: in such case, write "Continuation of Box No. VI", specify the number of the item corresponding to that earlier application and indicate at least one country party to the Paris Convention for the Protection of Industrial Property for which that earlier application was filed.

2. If, with regard to the precautionary designation statement contained in Box No. V, the applicant wishes to exclude any State(s) from the scope of that statement: in such case, write "Designation(s) excluded from precautionary designation statement" and indicate the name or two-letter code of each State so excluded.

3. If the applicant claims, in respect of any designated Office, the benefits of provisions of the national law concerning non-prejudicial disclosures or exceptions to lack of novelty: in such case, write "Statement concerning non-prejudicial disclosures or exceptions to lack of novelty" and furnish that statement below.

Box No. IV. Agent or Common Representative: (continued)

KOKULIS, Paul N.	BIRD, Donald J.	EDGEELL, G. Paul
LIPPITT, Raymond F.	ECCLESTON, Lynn E.	JAKOPIN, David A.
KNIGHT, G. Lloyd	GOWDEY, Peter W.	PAULSON, Mark G.
LOVE, Carl G.	LAZAR, Dale S.	KLIMA, Timothy J.
MARTIN, Edgar H.	PERRY, Glenn J.	McQUADE, Paul F.
	MORDUCH, Ruth N.	DZWONCZYK, Michael R.
JOYCE, Kevin E.	WHITE, Paul E., Jr.	SIRILLA, George M.
WISE, Roger R.	BENGTSOON, W. Patrick	BARUFKA, Jack s.
ZAITLEN, Richard H.	SMYRSKI, Steven W.	KIRKPATRICK, Anita M.
HESS, Adam R.	GLAZIER, Stephen C.	
FINKELSTEIN, Jay M.	NAGY, Paul G.	

All attorneys are partners of the firm of PILLSBURY MADISON & SUTRO, LLP. The address, telephone number, and facsimile number of all the above attorneys are as indicated in Box IV

Box No. VI PRIORITY CLAIM		<input type="checkbox"/> Further priority claim is indicated in the Supplemental Box.		
Filing date of earlier application (day/month/year)	Number of earlier application	Where earlier application is:		
		national application: country	regional application:* regional Office	international application: receiving Office
item (1) 12/November/1998 (12/11/98)	60/108,455	US		
item (2)				
item (3)				

☒ The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) (only if the earlier application was filed with the Office which for the purposes of the present international application is the receiving Office) identified above as item(s): (1)
 * Where the earlier application is an ARIPO application, it is mandatory to indicate in the Supplemental Box at least one country party to the Paris Convention for the Protection of Industrial Property for which that earlier application was filed (Rule 4.10(b)(ii)). See Supplemental Box.

Box No. VII INTERNATIONAL SEARCHING AUTHORITY

Choice of International Searching Authority (ISA)
 (if two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used):

ISA/EP

Request to use results of earlier search; reference to that search (if an earlier search has been carried out by or requested from the International Searching Authority):

Date (day/month/year) Number Country (or regional Office)

Box No. VIII CHECK LIST: LANGUAGE OF FILING

This international application contains the following number of sheets:

request : 5
 description (excluding sequence listing part) : 27
 claims : 6
 abstract : 1
 drawings : 2
 sequence listing part of description :
 Total number of sheets : 41

This international application is **accompanied** by the item(s) marked below:

- ☒ fee calculation sheet
- ☐ separate signed power of attorney
- ☐ copy of general power of attorney; reference number, if any:
- ☐ statement explaining lack of signature
- ☐ priority document(s) identified in Box No. VI as item(s):
- ☐ translation of international application into (language):
- ☐ separate indications concerning deposited microorganism or other biological material
- ☐ nucleotide and/or amino acid sequence listing in computer readable form
- ☒ other (specify): Transmittal letter & Postcard

Figure of the drawings which should accompany the abstract:

Language of filing of the international application:

English

Box No. IX SIGNATURE OF APPLICANT OR AGENT

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request).

Kendrew H. Colton

For receiving Office use only		(09.11.99)
1. Date of actual receipt of the purported international application:	09 NOV 1999	2. Drawings:
3. Corrected date of actual receipt due to later but timely received papers or drawings completing the		<input type="checkbox"/> received:

If two or more International Searching Authorities are competent, indicate the Authority chosen (the two-letter code may be used): ISA/EP	<input type="checkbox"/> International search copy is required until search fee is paid
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METHOD FOR THE SYNTHESIS OF ENERGETIC THERMOPLASTIC ELASTOMERS IN NON-HALOGENATED SOLVENTS

BACKGROUND OF THE INVENTION

5

1. Field of the Invention

This invention relates to a method of synthesizing energetic thermoplastic elastomers which are useful as binders of high energy compositions, such as rocket motor propellants, gun propellants, explosive munitions, gas generants of vehicle supplemental restraint systems, or the like.

10

2. Description of the Related Art

Solid high energy compositions, such as propellants, explosives, gas generants, and the like comprise solid particulates, such as fuel particulates and/or oxidizer particulates, dispersed and immobilized throughout a polymeric binder matrix.

15

Conventional solid composite propellant binders utilize cross-linked elastomers in which prepolymers are cross-linked by chemical curing agents. As outlined in detail in U.S. Patent No. 4,361,526, there are important disadvantages to using cross-linked elastomers as binders. Cross-linked elastomers must be cast within a short period of time after addition of the curative, which time period is known as the "pot life". Disposal of a cast, cross-linked propellant composition is difficult, and usually is accomplished by burning, which poses environmental problems. Furthermore, current state-of-the-art propellant compositions have serious problems that include their use of nonenergetic binders which have lower performance and high end-of-mix viscosities.

20

In view of the inherent disadvantages associated with the use of cross-linked elastomeric polymers as binder materials, there has been considerable interest in developing thermoplastic elastomers suitable as binders for solid, high energy

being processible below about 120°C, it being desirable that a thermoplastic elastomeric polymer for use as a binder in a high energy system have a melting temperature of between about 60°C and about 120°C. The melting temperature is desirably at least about 60°C because the propellant composition may be subject to somewhat elevated temperatures during storage and transport, and significant softening of the propellant composition at such elevated temperatures is unwanted. The setting of the melting temperature at not more than about 120°C is determined by the instability, at elevated temperatures, of many components which ordinarily go into high energy compositions, particularly oxidizer particulates and energetic plasticizers. Many thermoplastic elastomers exhibit high melt viscosities which preclude high solids loading and many show considerable creep and/or shrinkage after processing. Thermoplastic elastomers typically obtain their thermoplastic properties from segments that form glassy domains which may contribute to physical properties adverse to their use as binders. Crosslinkable thermoplastic elastomers are block copolymers with the property of forming physical cross-links at predetermined temperatures. One thermoplastic elastomer, e.g., Kraton, brand TPE, obtains this property by having the glass transition point of one component block above room temperature. At temperatures below 109°C, the glassy blocks of Kraton form glassy domains and thus physically cross-link the amorphous segments. The strength of these elastomers depends upon the degree of phase separation. Thus, it remains desirable to have controlled, but significant, immiscibility between the two types of blocks, which is a function of their chemical structure and molecular weight. On the other hand, as the blocks become more immiscible, the melt viscosity increases, thus having a deleterious effect on the processibility of the material.

Above-mentioned U.S. Patent No. 4,361,526 proposes a thermoplastic elastomeric binder which is a block copolymer of a diene and styrene, the styrene blocks providing a meltable crystal structure and the diene blocks imparting rubbery

processed with a volatile organic solvent. Solvent processing is undesirable inasmuch as the dissolved composition cannot be cast in a conventional manner, e.g., into a rocket motor casing. Furthermore, solvent-based processing presents problems with respect to removal and recovery of solvent.

5 The preparation of energetic thermoplastic elastomers prepared from polyoxetane block copolymers has been proposed in U.S. Patent No. 4,483,978 to Manser and U.S. Patent No. 4,806,613 to Wardle ("the '613 patent"), the complete disclosures of which are incorporated herein by reference to the extent that these
10 disclosures are compatible with this invention. According to the latter, these materials overcome the disadvantages associated with conventional cross-linked elastomers such as limited pot-life, high end-of-mix viscosity, and scrap disposal problems.

 The thermoplastic materials proposed by the '613 patent involve elastomers having both (A) and (B) blocks, each derived from cyclic ethers, such as oxetane and oxetane derivatives and tetrahydrofuran (THF) and tetrahydrofuran derivatives. The
15 monomer or combination of monomers of the (A) blocks are selected for providing a crystalline structure at usual ambient temperatures, such as below about 60°C, whereas the monomer or combination of monomers of the (B) blocks are selected to ensure an amorphous structure at usual ambient temperatures, such as above about -20°C. Typical of these materials is the random block copolymer (poly(3-
20 azidomethyl-3-methyloxetane)-poly(3,3-bis(azidomethyl)oxetane), also known as poly(AMMO/BAMO). These block copolymers have good energetic and mechanical properties. Additionally, the block copolymers can be processed without solvents to serve as binders in high performance, reduced vulnerability explosive, propellant, and gas generant formulations. Advantageously, the block copolymers exhibit good
25 compatibility with most materials used in such energetic formulations.

 The processing techniques disclosed in the '978 and '613 patents

drawbacks have been associated with the use of the halogenated solvents disclosed in the '978 and '613 patents. One drawback is the detrimental impact that halogenated solvents have on the environment. Another drawback of halogenated solvents is attributable to the additional drying steps which the pre-polymer blocks are subject to after their formation. The pre-polymer blocks are typically dried either with chemical drying agent, e.g., desiccants followed by filtration or by the azeotropic removal of water. The azeotropic removal of water is performed with toluene, which is different from the solvent selected for linking the pre-polymer blocks. The performance of an additional drying step and the use of different solvents in the azeotropic drying step and the linking step complicates processing and increases overall processing time. Moreover, toluene does not completely dissolve the end-capped blocks prior to the linking reaction and can interfere with the end-capping and linking catalysts. Yet another drawback associated with halogenated solvents is the relatively low concentrations of pre-polymer blocks and linking compounds that may be loaded in halogenated solvents for processing. The loading of the thermoplastic elastomer ingredients is limited by the solubility of the ingredients in the solvent. For example, the currently used process for forming thermoplastic elastomers by linking energetic polyether diols and diisocyanates typically use approximately 30-40% by weight solutions of the reactants in dichloromethane and 0.1% by weight tin catalyst. Additionally, completion of the reaction in halogenated solvents typically takes several days to a week.

United States Patent No. 4,393,199 to Manser describes the use of a non-halogenated solvent, nitromethane, during cationic polymerization of cyclic ethers. However, it has been found that cyclic ether pre-polymer blocks are not sufficiently soluble in nitromethane to adequately link the pre-polymer blocks once they are formed.

It would therefore be a significant advancement in the art to provide a

drawbacks associated with halogenated solvents while reducing processing time and increasing productivity.

SUMMARY OF THE INVENTION

5 It is, therefore, an object of this invention to provide a method for the synthesis of energetic thermoplastic elastomers that addresses the aforementioned problems associated with the related art and realizes the advancement expressed above.

10 In accordance with the principles of this invention, these and other objects are attained by a method of synthesizing an energetic thermoplastic elastomer binder that is in a solid state at room temperature and is derived from A blocks which are crystalline at temperatures below about 60°C and B blocks are amorphous at temperatures above about -20°C. The A blocks may include one or more polyethers derived from monomers of oxetane derivatives and/or tetrahydrofuran derivatives. The B blocks may include one or more polyethers derived from monomers of oxetane
15 and its derivatives, tetrahydrofuran and its derivatives, and/or oxirane and its derivatives. The polyoxetane blocks A and polyoxirane blocks B may be linked by end-capping the blocks with diisocyanates and linking the end-capped blocks with difunctional linking chemicals in which each of the two terminal functional groups are reactive with an isocyanate moiety of the diisocyanate.

20 In accordance with one embodiment of this method, the A and B blocks are dissolved into solution comprising one or more non-halogenated solvents. The solvent or solvents selected preferably are capable of dissolving more than 25% by weight of the blocks (based on total weight of the solvents and blocks) into solution, more preferably at least 35% by weight into solution, and still more preferably 50%
25 by weight into solution. The solvents preferably do not interfere with the end capping

and ketones. Tetrahydrofuran is the preferred solvent because of its excellent solubility. The A and B blocks are mixed together at approximately the stoichiometric ratios that the blocks are intended to be present in the energetic thermoplastic elastomer. The solution is then dried by azeotropic removal of water with excess solvent. The A and B blocks are end-capped in the solvent with one or more diisocyanates. The end-capping may be performed prior or subsequent to the mixing step, but subsequent to the drying step. The diisocyanate preferably has one isocyanate moiety which is more reactive, preferably at least about five times as reactive, with the terminal hydroxyl group of each of the blocks than the other isocyanate moiety, whereby the more reactive isocyanate moiety tends to react with the terminal-hydroxyl groups of the blocks, leaving the less reactive isocyanate moiety free and unreactive. The mixture is reacted with a chain extender having two isocyanate-reactive groups that are sufficiently unhindered to react with the free and unreacted isocyanate groups of the end-capped blocks. In this manner, the end-capped blocks are linked, but not crosslinked, to form a thermoplastic elastomer.

It is still a further object of this invention to provide a method for making propellants, especially rocket propellants and gun propellants, explosives, gas generants, or the like containing an energetic thermoplastic elastomer binder by procedures including the above-discussed method.

These and other objects, features, and advantages of the present invention will become apparent from the accompanying drawings and following detailed description which illustrate and explain, by way of example, the principles of this invention.

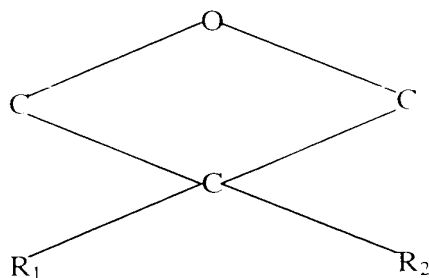
BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings are provided to facilitate an understanding of the principles of this invention. In such drawings, FIGS. 1 and 2 are graphs showing the properties of a thermoplastic elastomer prepared in accordance with an embodiment

DETAILED DESCRIPTION OF THE INVENTION

The thermoplastic elastomer $(AB)_n$ polymers of this invention include A blocks which are crystalline at temperatures below about 60°C , preferably at temperatures below about 75°C , and B blocks which are amorphous at temperatures down to about -20°C . Each of the A and B blocks are polyethers derived from cyclic ethers. Specifically, the A blocks are derived from monomers of oxetane derivatives and/or THF derivatives. The B blocks are derived from monomers of oxetane and its derivatives, THF and its derivatives, and/or monomers of oxirane and its derivatives, preferably energetic oxirane derivatives. The polymers melt at temperatures between about 60°C and about 120°C , and more preferably between about 75°C and about 100°C . The A and B blocks are mutually miscible in the melt. Consequently, the melt viscosity of the block copolymer decreases rapidly as the temperature is raised above the melting point, whereby high energy formulations may include high solids content, e.g., up to about 95% by weight of solid particulates, and can be easily processed. The invention also includes other thermoplastic elastomer block structures, such as ABA tri-block polymers and A_nB star polymers. Contributing to the miscibility of the A and B blocks is their similar chemical structure.

Oxetane monomer units that may be used in forming the A and B blocks of the present invention have the general formula:



wherein the R_1 and R_2 groups are the same or different and are selected from moieties having the general formula: $-(CH_2)_nX$, where n is 0-10 and X is selected from the group consisting of $-H$, $-NO_2$, $-CN$, $-Cl$, $-F$, $-O$ -alkyl, $-OH$, $-I$, $-ONO_2$, $-N(NO_2)$ -alkyl, $-C\equiv CH$, $-Br$, $-CH=CH(H \text{ or alkyl})$, $-CO_2$ -(H or alkyl), $-N(H \text{ or alkyl})_2$,

5 $-O-(CH_2)_{1-5}-O-(CH_2)_{0-8}-CH_3$, and N_3 .

Examples of oxetane derivatives that may be used in forming the A blocks in accordance with this invention are generally symmetrically-substituted oxetanes including, but are not limited to, the following: BEMO (3,3-bis(ethoxymethyl)oxetane), BCMO (3,3-bis(chloromethyl)oxetane), BMMO (3,3-bis(methoxymethyl)oxetane), BFMO (3,3-bis(fluoromethyl)oxetane), BAOMO (3,3-bis(acetoxymethyl)oxetane), BHMO (3,3-bis(hydroxymethyl)oxetane), BMEMO (3,3-bis(methoxyethoxymethyl)oxetane), BIMO (3,3-bis(iodomethyl)oxetane), BNMO (3,3-bis(nitratomethyl)oxetane), BMNAMO (3,3-bis(methylnitraminomethyl)oxetane), and BAMO (3,3-bis(azidomethyl)oxetane).

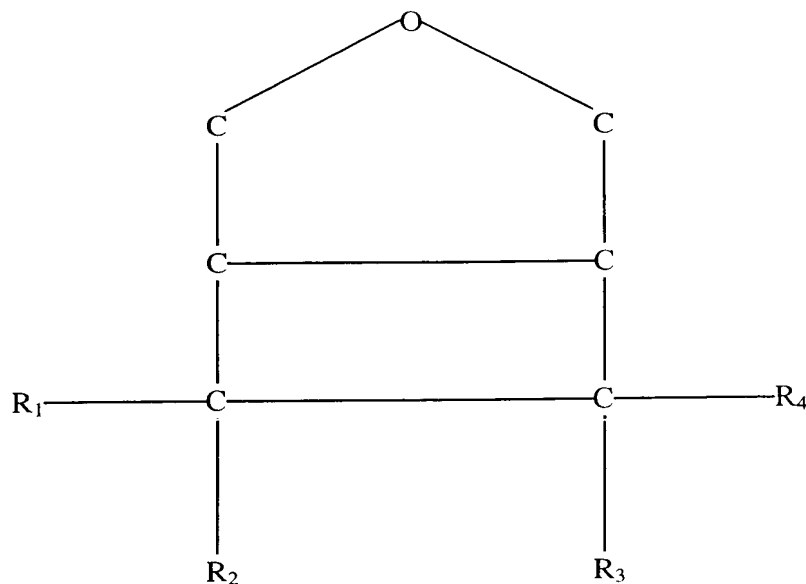
15 Examples of oxetanes derivatives that may be used in forming the B blocks in accordance with this invention are generally unsymmetrically-substituted oxetanes including, but are not limited to, the following: HMMO (3-hydroxymethyl-3-methyloxetane), OMMO (3-octoxymethyl-3-methyloxetane), CMMO (3-chloromethyl-3-methyloxetane), AMMO (3-azidomethyl-3-methyloxetane), IMMO (3-iodomethyl-3-methyloxetane), PMMO (3-propynomethylmethyloxetane), NMMO (3-nitratomethyl-3-methyloxetane), and MNAMMO (3-methylnitraminomethyl-3-methyloxetane).

20 Tetrahydrofuran monomer units that may be used in forming the blocks of the present invention have the general formula:

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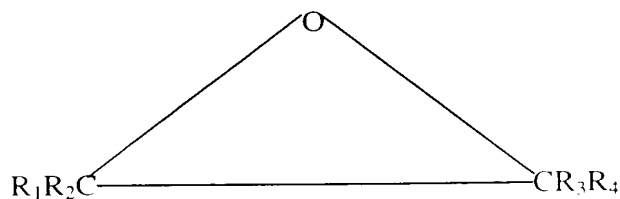


20

wherein the R_1 - R_4 groups are the same or different and are selected from moieties set forth above in connection with the description of suitable oxetane derivatives.

Oxirane monomer units used in forming the B blocks of the present invention have the general formula:

25



30

wherein R_1 and R_3 are independently selected from hydrogen and methyl, and R_2 and R_4 are independently selected from hydrogen, alkyl containing from 1 to 10 carbon atoms, chloroalkyl and bromoalkyl containing 1 to 2 carbon atoms, and nitratoalkyl, nitratoalkoxyalkyl, nitroalkyl, nitroalkoxyalkyl, azidoalkyl, azidoalkoxyalkyl.

fluoronitroalkyl, and fluoronitroalkoxyalkyl containing 1 to 5 carbon atoms provided that at least one of R_1 to R_4 is not hydrogen.

Examples of energetic oxiranes that may be used in forming the B blocks in accordance with this invention include, but are not limited to glycidyl azide polymers (C₃H₅N₃O) (GAP), especially difunctional GAP, and poly(glycidyl nitrate) (C₃H₅NO₄) (PGN). These polymers have a glass transition temperature below about -20°C and are amorphous at temperatures above -20°C.

Forming thermoplastic elastomers in accordance with the invention involves (1) formation of at least one polyether-derived homopolymer, copolymer, or terpolymer serving as the A blocks and crystalline in nature with a relatively elevated melting point, i.e., between about 60°C and about 120°C, preferably near 80°C and (2) formation of at least one polyether-derived homopolymer, copolymer, or terpolymer serving as the B blocks and amorphous in structure with a glass transition temperature (T_g) below about -20°C.

The selection of the A block may be made based on the properties desired for the intended application of the thermoplastic elastomer. Examples of preferred crystalline A blocks include blocks possessing high energy density, such as those formed from BAMO and/or BMNAMO monomers. Melting temperature and ether oxygen content are additional factors that may be taken into consideration in selecting the monomers.

The properties of the block polymer depends upon the molecular weights of the individual blocks and the total molecular weights. Typically the A blocks have number average molecular weights ranging from about 3000 to about 8000, whereas the B blocks have number average molecular weights ranging from about 3000 to about 15,000. The weight ratio of A blocks to B blocks is preferably between about

15:85 to about 40:60. The preferred sizes of the A and B blocks for any particular binder application may be empirically determined.

The thermoplastic elastomers of this invention preferably are in a solid state at room temperature, have a weight average molecular weight of at least 40,000, more preferably at least 60,000, still more preferably at least 80,000, and a number average molecular weight of at least 10,000, more preferably at least 12,000, still more preferably at least 15,000.

Thermoplastic elastomers produced in accordance with the present invention may be admixed with other components of a high energy formulation, such as a propellant formulation. The binder system, in addition to the thermoplastic elastomers, may optionally contain one or more plasticizers for improving the resistance of the thermoplastic elastomer to hardening at low temperatures, which may be included at a plasticizer-to-thermoplastic elastomer weight ratio of up to about 1:1. Suitable high energy plasticizers include glycidyl azide polymer (GAP), nitroglycerine, butanetriol trinitrate (BTTN), alkyl nitratomethyl nitramines, trimethylolethane trinitrate (TMETN), diethylene glycol dinitrate, triethylene glycol dinitrate (TEGDN), bis(dinitropropylacetal/-bis(dinitropropyl)formal (BDNPA/F), and mixtures thereof. Inert plasticizers can also be used. Representative inert plasticizers include, by way of example, dioctyladipate (DOA), isodecylperlargonate (IDP), dioctylphthalate (DOP), dioctylmaleate (DOM), dibutylphthalate (DBP), oleyl nitrile, triacetin, and combinations thereof. The binder system may also contain a minor amount of a wetting agent or lubricant that enables higher solids loading.

The solids content of the high energy composition generally ranges from about 50 wt% to about 95 wt%, higher solids loading generally being preferred so long as such loading is consistent with structural integrity. The solids include fuel material particles and powders (collectively referred to herein as particulates), such as

aluminum, magnesium, boron, and beryllium. Representative oxidizers and co-oxidizers include ammonium perchlorate; hydroxylammonium nitrate (HAN); ammonium dinitramide (ADN); hydrazinium nitroformate; ammonium nitrate; nitramines such as cyclotetramethylene tetranitramine (HMX) and cyclotrimethylene trinitramine (RDX), 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-
5 hexaazatetracyclo[5.5.0.0^{5,9}.0^{3,11}]-dodecane or 2,4,6,8,10,12-hexanitrohexaazaisowurtzitane (CL-20 or HNIW), and/or 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo[5.5.0.0^{5,9}.0^{3,11}]dodecane (TEX), and any combination thereof. In addition, the high energy composition may include minor amounts of
10 additional components known in the art, such as bonding agents, burn rate modifiers, ballistic modifiers (e.g., lead), etc.

The thermoplastic elastomer may be mixed with the solids and other components of high energy formulation at temperatures above its melting temperature. Blending may be done in conventional mixing apparatus. Because of
15 the low viscosities of the molten polymer, no solvents are required for blending or other processing, such as extrusion.

An important advantage of having a binder which is meltable is that the elastomer from an outdated device containing can be melted down and reused. At the time of such remelting, the binder might be reformulated, e.g., by addition of
20 additional fuel or oxidizer particulates. Accordingly, the thermoplastic elastomer provides for its eventual recycle, as opposed to the burning required for disposal of cross-linked compositions. Because the "pot life" of the thermoplastic propellant exceeds that which would reasonably be required of a propellant or explosive formulation, if any problems develop during casting, the process can be delayed as
25 long as is reasonably necessary, merely by maintaining the formulation in a molten state.

The oxetane homopolymer blocks may be formed according to the cationic polymerization technique taught by Manser in U.S. Patent No. 4,393,199, the complete disclosure of which is incorporated herein by reference. The oxirane homopolymer blocks may be formed according to the technique taught in U.S. Patent
5 No. 5,120,827, the complete disclosure of which is incorporated herein by reference. The technique employs an adduct of a substance such as a diol, e.g., 1,4-butane diol (BDO), and a catalyst for cationic polymerization, e.g., BF_3 -etherate. This adduct forms with the oxetane monomer an initiating species which undergoes chain extension until n moles of monomer have been incorporated in the molecule, n being
10 the ratio of monomers to adduct present. By adjusting the ratio of monomers to adduct present, the average molecular weight of the polymer which forms may be adjusted. If two or more monomers are present, incorporation of the monomers will be generally random but may depend upon the relative reactivities of the monomers in the polymerization reaction.

15 Another suitable catalyst system includes co-catalytically effective quantities of one or more triethoxonium salts and one or more alcohols, as disclosed in U.S. Application No. 08/233,219, the complete disclosure of which is incorporated herein by reference to the extent that the disclosure is compatible with this invention. Examples of triethoxonium salts include triethoxonium hexafluorophosphate,
20 triethoxonium hexafluoroantimonate, and triethoxonium tetrafluoroborate.

It is understood that although the isocyanate-reactive terminal functional groups of the blocks are referred to herein as being hydroxyl groups, the isocyanate-reactive functional groups may also be amines, amides, and/or carboxyl groups.

The crystalline polyoxetane A blocks and amorphous B blocks, i.e., the
25 respective prepolymers, are each end-capped together or separately with one or more diisocyanates. The end-capped A and B blocks are mixed together and joined by a

sufficiently unhindered to allow them to react with the free isocyanate moieties of the end-capped copolymers and thereby join the blocks together.

Oxetane, THF, and oxirane polymer blocks normally have terminal isocyanate-reactive (e.g., hydroxyl) functions which are end-capped with the diisocyanates in accordance with the invention. Preferably, a first one of the isocyanate moieties of the end-capping compound is substantially more reactive with the terminal-hydroxyl moieties of the polymer blocks than the other (e.g., second) isocyanate moiety. One of the problems with linking these types of polymer blocks is that substituted oxetane-derived hydroxyl end groups units have neopentyl structures, whereby the terminal primary hydroxyl moieties are substantially hindered and therefore less reactive. The blocks derived from the oxirane derivatives are secondary alcohols, making their hydroxyl groups less reactive than the primary hydroxyl group of the oxetane-derived A-block. The diisocyanate preferably is selected so that one of the isocyanate groups is capable of reacting with a hydroxyl-group of the polymer blocks while the other isocyanate moiety remains free and unreacted. Diisocyanates are preferably used because isocyanates of higher functionality would result in undesirable levels of cross-linking. The different reactivities of the isocyanate moieties is desirable to ensure that substantial chain extension through linking of like blocks does not occur. Thus, for purposes of this invention, one isocyanate moiety of the diisocyanate should preferably be approximately five times more reactive with terminal hydroxyl groups of oxetane and oxirane blocks than the other group. Preferably one isocyanate moiety is at least about ten times more reactive than the other.

One diisocyanate which is especially useful for purposes of the invention is 2,4-toluene diisocyanate (TDI) in which the isocyanate moiety in the 4-position is substantially more reactive with hindered terminal hydroxyl moieties than the isocyanate moiety in the 2-position. Isophorone diisocyanate (IPDI) is suitable for

not worked well include diphenylmethylene diisocyanate (MDI) and hexamethylene diisocyanate (HDI).

In the end-capping reaction, the diisocyanate is used at an approximately stoichiometric molar amount relative to terminal hydroxyl groups on the polymer chain. Thus, if the polymer chain has a pair of terminal hydroxyl groups, approximately two molar equivalents, e.g., 1.75-2.2 molar equivalents of diisocyanate are used. In the ideal reaction, all of the more reactive isocyanate moieties would react with terminal hydroxyl groups, leaving all of the less reactive isocyanate moieties free. Practically, not all of the diisocyanate reacts in this manner, and some chain extension does occur. Thus, the end-capping reaction may be maximized for particular polymer chains by some adjustment in the relative molar ratios of polymer block and diisocyanate.

In one variant embodiment, the A blocks and B blocks are reacted separately with the diisocyanate, so that there is no competition of the blocks for diisocyanate molecules and each separate end-capping reaction may be carried to substantial completion. The diisocyanate may react more rapidly with one block than the other, but this difference can be compensated for by a longer reaction time with the slower reacting block. The reactivity of the terminal hydroxyl groups varies according to steric factors and also according to side-chain moieties. Energetic oxetanes, for example, generally have side-chain moieties that are electron-withdrawing, making their terminal hydroxyl groups less reactive. Once end-capped with diisocyanate, the reactivities of the polymers for linking purposes is essentially dependent only upon the reactivity of the free isocyanate, not on the chemical makeup of the polymer chain itself. Thus end-capped (A) blocks are substantially as reactive as end-capped (B) blocks.

The end-capping reaction is promoted by a suitable urethane catalyst. A

preferably two labile groups, such as chloride or acetate, bound directly to the tin. Suitable tin catalyst include diphenyl tin dichloride, dibutyl tin dichloride, dibutyl tin dilaurate, dibutyl tin diacetate. Tertiary amine catalysts may also be used.

5 The linking compound is one which has two functional groups which are sufficiently unhindered to react with the free isocyanate moieties on the end-capped blocks so as to link A blocks to B blocks, A blocks to A blocks, and B blocks to B blocks in a urethane reaction. Preferred functional groups are hydroxyl groups, although amine, amide, and carboxyl groups, and mixtures thereof also react in a urethane reaction. Primary functional groups are preferred. The linking compound
10 may be a short, straight carbon chain having terminal hydroxyl groups, e.g., 1,4-butanediol, 1,3-propanediol, ethylene glycol, and 1,6-hexanediol. The linking compound should also be miscible with and rapidly dissolve in the non-halogenated solvent so as to ensure chain extension without unwanted amounts of cross-linking.

Alternatively, the linking compound may be an oligomer, especially a
15 urethane oligomer, having two functional groups which are sufficiently unhindered to react with the free isocyanate moieties on the end-capped blocks so as to link A blocks to B blocks, A blocks to A blocks, and B blocks to B blocks via a urethane reaction. Preferred functional groups of the oligomer are hydroxyl groups, although amine, amide, and carboxyl groups, and mixtures thereof also react in a urethane
20 reaction. Primary functional groups are preferred.

An oligomeric glycol containing urethane moieties is preferably used to react the free isocyanate moieties on the end-capped blocks. The oligomeric glycol may be prepared from a mixture of one or more diisocyanates and an excess amount of one or more diols. The diisocyanate(s) and diol(s) selected and the ratio of these reagents
25 may be varied to tailor the properties of the thermoplastic elastomer. The diol-to-diisocyanate molar ratio is preferably selected to be between 5:1 to 5:4, more

linking of the isocyanate-capped prepolymers, and improve the thermomechanical properties of the final thermoplastic elastomer. A suitable urethane reaction catalyst promotes the reaction between the diisocyanate(s) and diol(s) to form oligomers. The catalysts discussed above in connection with the linking of the A and B blocks are
5 suitable for this purpose. Representative diols that may be selected for preparing the difunctional oligomer include, by way of example, unbranched aliphatic diols having 2 to 7 carbon atoms, such as ethylene glycol, propylene glycol, butylene glycol; and cycloaliphatic diols such as 1,4-cyclohexanedimethanol, and any combination thereof. Representative diisocyanates for preparing the difunctional oligomer include, by way
10 of example, aliphatic diisocyanates such as hexane diisocyanate, and aryl diisocyanates such as methylene-bis(4-phenyl isocyanate), phenylene diisocyanate, toluene diisocyanate, and xylylene diisocyanate, and any combination thereof. Preferably, the difunctional oligomer has a number average molecular weight M_n of from 350 to 900.

15 It is to be appreciated that a wide variety of difunctional compounds maybe used to link the end-capped blocks.

As in the end-capping reaction, some solvent is preferably used, as is a catalyst, such as described above. Conveniently, the reaction mixtures of the A blocks and B blocks may be mixed together without prior separation of the blocks
20 from their respective end-capping reaction mixtures. The linking compound can be added directly to this mixture of A and B blocks. The catalyst is thereby already present when the linking compound is added.

The linking compound is added in an amount such that the total number of linking-compound functional groups approximately equals the total number of free
25 isocyanate groups of the end-capped polymer blocks. Thus, to provide an $(AB)_n$ polymer with multiple blocks in each chain, the linking compound to polymer block

molar ratio is in the range of 0.9-1.1, e.g., 1.0. Accordingly, optimal molar ratios of blocks and linking chemicals may have to be empirically determined.

The end-capping reaction and linking reaction are carried out in a suitable non-halogenated solvent, e.g., one which dissolves the polymer and does not react
5 with the free isocyanate moieties. Although insubstantial amounts of halogenated solvent may be present, the solution is preferably completely free of any halogenated solvent. The non-halogenated solvent should not react in the urethane reaction and forms an azeotrope with water. Suitable dry solvents include cyclic ethers such as tetrahydrofuran (THF) and 1,4-dioxane; non-cyclic ethers such as ethylene glycol
10 dimethyl ether; ketones such as methyl ethyl ketone ("MEK"); and esters such as ethyl acetate. Of these, THF is preferred because of its excellent solubility characteristics.

In a preferred embodiment, the solvent forms an azeotrope with water. In this preferred embodiment, after the blocks are dissolved in excess non-halogenated solvent, the solution may be dried by azeotropic distillation of the solvent, and
15 optionally further concentrated, e.g., via distillation, in the solution to increase the volumetric loading and reaction rate. The blocks then may be end-capped, separately or together, and linked in the same or a different non-halogenated solvent. By distilling off excess solvent to remove water, subsequent reaction with a diisocyanate may proceed without significant interference from competing reactions between the
20 isocyanate moieties and water. Additionally, the solution remains homogeneous and further distillation serves to concentrate the polymer solution, producing higher reaction rates and requiring less reactor capacity. The reaction rates may be improved by conducting the end-capping reaction at elevated temperatures, such as 30°C to 80°C, more preferably 40°C to 60°C. The process may be conducted by a batch or
25 continuous method. For example, the prepolymer and catalyst solution may be continuously fed through a mixer/extruder into which is injected a diisocyanate and a diol at appropriate rates and positions so that urethane linking occurs within the

extruder and energetic thermoplastic elastomer is continuously produced for processing.

In the end-capping and block linking steps, the reaction can be followed with NMR and IR. With NMR, the urethane-forming reaction can be followed through the methylene groups on the polymer adjacent to the terminal hydroxyl groups. With IR, the change from isocyanate to urethane can be directly followed.

Synthesis of polyoxetanes is described in U.S. Patent Nos. 4,483,978 and 4,806,613, the complete disclosures of which are incorporated herein by reference to the extent that these disclosures are compatible with the present invention.

The invention will now be described in greater detail by way of the following examples, which are not to be construed as exhaustive as to the scope of this invention.

As referred to herein, "dry" means that less than 1 wt% water was present.

For the following experiments, poly(azidomethyloxirane) was supplied by 3M Speciality Chemicals of St. Paul, MN (Lot L-12564). Unless otherwise specified, all other materials were obtained from Aldrich of Milwaukee, WI.

EXAMPLE 1 (poly(3,3-bis(azidomethyl)oxetane))

A 5 liter jacketed flask equipped with a mechanical stirrer was charged with 600 grams of tribromoneopentylalcohol (AmeriBrom, Inc. of New York), 1200 ml of toluene, and 6 grams of tetrabutylammonium bromide. The mixture was cooled to 12°C and 193 grams of sodium hydroxide was added dropwise as a 40 wt% solution keeping the temperature at 12°C. After 36 hours the reaction mixture was washed with water until the pH was less than 9 to obtain the crude product which was distilled to obtain 3,3-bis(bromomethyl)oxetane at 65% yield.

A 5 liter jacketed flask equipped with a mechanical stirrer was charged with 1450 grams of the 3,3-bis(bromomethyl)oxetane and 1720 ml of toluene. The mixture was stirred and heated to 60°C before 1600 ml of water, 14.7 grams of tetrabutylammonium bromide, and 862 grams of sodium azide were added. After 24 hours, the reaction mixture was cooled to room temperature and washed three times with 2000 ml of water. The toluene and water were removed from the organic layer by distillation to give pure 3,3-bis(azidomethyl)oxetane at 85% yield.

Under an argon atmosphere, 14.94 grams of butane diol was added to a flame dried 5 liter round-bottomed flask charged with 1340 ml of dry methylene chloride. To this mixture, 11.77 grams of borontrifluoride-etherate was added and the reaction was allowed to proceed for one hour at room temperature. The reactor was then cooled to -10°C and 937.78 grams of the 3,3-bis(azidomethyl)oxetane was added. The solution was allowed to come to room temperature and left to react for three days. The reaction was then quenched by the addition of 50 ml of saturated brine solution. The organic phase was separated off and washed with 100 ml of 10 wt% sodium bicarbonate solution before the solvent was removed on a rotovapor. The resulting liquid was then poured into 5 liters of methanol to precipitate the polymer, which was filtered from the solution and dried under vacuum at 30°C.

EXAMPLE 2 (poly(3-azidomethyl-3-methyloxetane))

A 5 liter jacketed flask equipped with a mechanical stirrer was charged with 1062 grams of sodium azide, 1972 ml of water, and 2450 grams of 3-bromomethyl-3-methyloxetane (supplied by AmeriBrom, Inc. of New York). This mixture was brought to reflux with vigorous mixing. After 48 hours the mixture was cooled to room temperature. The organic layer was separated off and washed three times with 1000 ml of water before being dried over molecular sieves to yield pure 3-azidomethyl-3-methyloxetane at 85% yield.

Under an argon atmosphere, 14.94 grams of butane diol was added to a flame dried 5 liter round-bottomed flask charged with 1.340 ml of dry methylene chloride. To this mixture, 11.77 grams of borontrifluoride-etherate was added and the reaction was allowed to proceed for one hour at room temperature. The reactor was then
5 cooled to -10°C and 937.78 grams of the 3-azidomethyl-3-methyloxetane was added. The solution was allowed to come to room temperature and left to react for three days. The reaction was then quenched by the addition of 50 ml of saturated brine solution. The organic phase was separated off and washed with 100 ml of 10 wt% sodium
10 bicarbonate solution before the solvent was removed on a rotovapor. The resulting liquid was then poured into 5 liters of methanol to precipitate the polymer, which was filtered from the solution and dried under vacuum at 30°C.

EXAMPLE 3 (Random block copolymer of poly(3-azidomethyl-3-methyloxetane) and poly(3,3-bis(azidomethyl)oxetane) in THF)

In a one liter round bottom flask, 65 grams of dry difunctional poly(3-
15 azidomethyl-3-methyloxetane) with a hydroxyl equivalent weight of 3121 and 35 grams of dry poly(3,3-bis(azidomethyl)oxetane) with a hydroxyl equivalent weight of 3235 were dissolved in 650 grams of dry tetrahydrofuran. The solution was concentrated and dried by evaporation of the tetrahydrofuran under reduced pressure via a rotovapor until 100 grams of the solvent remained. To this solution, 0.1 grams
20 of diphenyltin dichloride and 5.41 grams of toluene-2,4-diisocyanate were added while stirring with a magnetic stirrer at ambient temperature and pressure. After 24 hours, 1.40 grams of butane-1,4-diol was added causing the solution to become steadily more viscous. After another 24 hours, the solution was poured into methanol in a volume ratio of 1:5. The methanol was decanted off, and the precipitated
25 polymer was washed three times with fresh methanol (1:5 volume ratio) to give a rubbery granular product with the properties set forth below:

$M_n = 20480$

$M_w = 120500$

$$M_w/M_n = 5.9$$

$$E^{1.0} \text{ (psi)} = 754$$

$$\epsilon_m \text{ (\%)} = 204$$

$$\epsilon_f \text{ (failure) (\%)} = 229$$

5 $\sigma_m \text{ (psi)} = 180$

$$\sigma_m \text{ (corrected) (psi)} = 558$$

$$\text{Shore A} = 64$$

EXAMPLE 4 (Random block copolymer of poly(3-azidomethyl-3-methyloxetane) and poly(3,3-bis(azidomethyl)oxetane) in THF)

10 In a 100 ml round bottom flask, 6.5 grams of dry difunctional poly(3-azidomethyl-3-methyloxetane) with a hydroxyl equivalent weight of 3040 and 3.5 grams of dry poly(3,3-bis(azidomethyl)oxetane) with a hydroxyl equivalent weight of 3235 were dissolved in 60 ml of dry tetrahydrofuran. The solution was concentrated and dried by evaporation of the tetrahydrofuran under reduced pressure via a
15 rotovapor until 10 grams of the solvent remained. To this solution, 0.25 ml of dibutyltin dilaurate and 0.561 grams of toluene-2,4-diisocyanate were added while stirring with a magnetic stirrer at ambient temperature and pressure. After 15 minutes, 0.145 grams of butane-1,4-diol was added causing the solution to become steadily more viscous. After another 30 minutes, the solution was poured into
20 methanol in a volume ratio of 1:5. The methanol was decanted off, and the precipitated polymer was washed three times with fresh methanol (1:5 volume ratio) to give a rubbery granular product with the properties set forth below:

$$M_n = 15404$$

$$M_w = 67277$$

25 $M_w/M_n = 4.37$

EXAMPLE 5 (Random block copolymer of poly(3-azidomethyl-3-methyloxetane) and poly(3,3-bis(azidomethyl)oxetane) in 1,4-dioxane)

azidomethyl-3-methyloxetane) with a hydroxyl equivalent weight of 3040 and 3.5 grams of dry poly(3,3-bis(azidomethyl)oxetane) with a hydroxyl equivalent weight of 3235 were dissolved in 60 ml of dry 1,4-dioxane. The solution was concentrated and dried by evaporation of the 1,4-dioxane under reduced pressure via a rotovapor until
5 12 grams of the solvent remained. To this solution, 0.3 ml of dibutyltin dilaurate and 0.561 grams of toluene-2,4-diisocyanate were added while stirring with a magnetic stirrer at ambient temperature and pressure. After one hour, 0.145 grams of butane-1,4-diol was added causing the solution to become steadily more viscous. After another two hours, the solution was poured into methanol in a volume ratio of 1:5.
10 The methanol was decanted off, and the precipitated polymer was washed three times with fresh methanol (1:5 volume ratio) to give a rubbery granular product with the properties set forth below:

Mn = 21230

Mw = 116272

15 Mw/Mn = 5.48

EXAMPLE 6 (Random block copolymer of poly(3-azidomethyl-3-methyloxetane) and poly(3,3-bis(azidomethyl)oxetane) in ethyl acetate)

In a 500 ml round bottom flask, 18 grams of dry difunctional poly(3-azidomethyl-3-methyloxetane) with a hydroxyl equivalent weight of 3356 and 6
20 grams of dry poly(3,3-bis(azidomethyl)oxetane) with a hydroxyl equivalent weight of 3235 were dissolved in 200 ml of dry ethyl acetate. The solution was concentrated and dried by evaporation of the ethyl acetate under reduced pressure via a rotovapor until 34 grams of the solvent remained. To this solution at 40°C, 0.024 grams of diphenyltin dichloride and 1.26 grams of toluene-2,4-diisocyanate were added while
25 stirring with a magnetic stirrer. After one hour, 0.33 grams of butane-1,4-diol was added causing the solution to become steadily more viscous. After another 48 hours, the solution was poured into methanol in a volume ratio of 1:5. The methanol was

methanol (1:5 volume ratio) to give a rubbery granular product with the properties set forth below:

$M_n = 13880$

$M_w = 43310$

5 $M_w/M_n = 3.12$

EXAMPLE 7 (Random block copolymer of poly(3-azidomethyl-3-methyloxetane) and poly(3,3-bis(azidomethyl)oxetane) in THF)

In a 100 ml round bottom flask, 6.5 grams of dry difunctional poly(3-azidomethyl-3-methyloxetane) with a hydroxyl equivalent weight of 3040 and 3.5
10 grams of dry poly(3,3 bis(azidomethyl)oxetane) with a hydroxyl equivalent weight of 3235 were dissolved in 70 ml of dry tetrahydrofuran. The solution was concentrated and dried by evaporation of the tetrahydrofuran under reduced pressure via a rotovapor at 50°C until 5 grams of the solvent remained. To this solution at 50°C, 0.5
15 ml of dibutyltin dilaurate and 0.561 grams of toluene-2,4-diisocyanate were added while stirring with a magnetic stirrer. After three minutes, 0.145 grams of butane-1,4-diol was added causing the solution to become steadily more viscous. After another five minutes, the solution was diluted with 20 ml of tetrahydrofuran and 1 ml of methanol. This solution was then precipitate in methanol in a volume ratio of 1:5. The methanol was decanted off, and the precipitated polymer was washed three times
20 with fresh methanol (1:5 volume ratio) to give a rubbery granular product with the properties set forth below:

$M_n = 17350$

$M_w = 103231$

$M_w/M_n = 5.95$

25 EXAMPLE 8 (Random block copolymer of poly(azidomethyloxirane) and poly(3,3-bis(azidomethyl)oxetane))

In a 25 ml round bottom flask, a urethane oligomer was prepared by dissolving

solution 0.1 ml of dibutyltin dilaurate followed by 1.60 grams of butane-1,4-diol.
This reaction mixture was stirred for 1 hour at room temperature.

In a separate 250 ml round bottom flask, 17.94 grams of dry difunctional poly(azidomethyloxirane) with a hydroxyl equivalent weight of 1174 and 6.63 grams
5 of dry poly(3,3-bis(azidomethyl)oxetane) with a hydroxyl equivalent weight of 2390 were dissolved in 100 ml of dry tetrahydrofuran. The solution was concentrated and dried by evaporation of the tetrahydrofuran under reduced pressure via a rotovapor until 20 grams of the solvent remained. To this solution, 75 ml of dibutyltin dilaurate and 3.097 grams of toluene-2,4-diisocyanate were added while stirring with a
10 magnetic stirrer at ambient temperature and pressure. After one hour, the urethane oligomer was added to this solution, causing the solution to become steadily more viscous. After 20 minutes, the solution was too viscous to stir and was diluted with 20 ml of dry tetrahydrofuran and allowed to react for a further 20 minutes before being poured into methanol in a volume ratio of 1:5. The methanol was decanted off,
15 and the precipitated polymer was washed three times with fresh methanol (1:5 volume ratio) to give a rubbery granular product with the properties shown in FIGS. 1 and 2 and set forth below:

Mn = 26240

Mw = 175500

20 Mw/Mn = 6.69

Molecular weight distribution was determined by gel permeation chromatography using polystyrene standards, with the results shown in FIG. 1. The GPC trace in FIG. 1 demonstrates that the prepolymers were linked to produce a copolymer having a higher molecular weight and dispersivity than the homopolymer
25 blocks. The DMA trace in FIG. 2 shows the melt transition of random block (BAMO-GAP)_n at 75-80°C with a material modulus reducing only slowly before this point.

EXAMPLES 9-11 (Random block copolymer of poly(3-azidomethyl-3-methyloxetane) and poly(3,3-bis(azidomethyl)oxetane) linked with a urethane oligomer)

5 In a 500 ml round bottom flask, 45 grams of difunctional poly(3-azidomethyl-3-methyloxetane) with a hydroxyl equivalent weight of 3125 and 15 grams of poly(3,3-bis(azidomethyl)oxetane) with a hydroxyl equivalent weight of 3152 were dissolved in 300 ml of tetrahydrofuran. The solution was concentrated and dried by evaporation of the tetrahydrofuran or a rotovapor until a solution with 90 grams of solvent remained. To this solution 0.6 grams of dibutyltin dichloride and 3.34 grams
10 of toluene-2,4-diisocyanate was added and the mixture allowed to react for 3 hours to end-cap the prepolymer.

For Example 9, 0.22 grams of butanediol was added to one quarter of the isocyanate end-capped prepolymer mixture. The reaction was allowed to continue for 14 hours before it was precipitated with methanol in a volume ratio of 1:5. The
15 methanol was decanted off, and the precipitated polymer was washed three times with fresh methanol (1:5 volume ratio) to give a rubbery granular product.

For Example 10, a urethane oligomer was derived from a mixture of 2 ml of tetrahydrofuran, 0.42 grams of toluene-2,4-diisocyanate, 0.43 grams of butane-1,4-diol, and 0.1 grams of dibutyltin dichloride, which were allowed to react for one
20 hours. The urethane oligomer was then added to one quarter of the isocyanate end-capped prepolymer mixture and allowed to react for 14 hours before it was precipitated with methanol in a volume ratio of 1:5. The methanol was decanted off, and the precipitated polymer was washed three times with fresh methanol (1:5 volume ratio) to give a rubbery granular product.

25 For Example 11, a urethane oligomer was derived from a mixture of 2 ml of tetrahydrofuran, 0.83 grams of toluene-2,4-diisocyanate, 0.65 grams of butane-1,4-diol, and 0.1 grams of dibutyltin dichloride, which were allowed to react for one

hours. The urethane oligomer was then added to one quarter of the isocyanate end-capped prepolymer mixture and allowed to react for 14 hours before it was precipitated with methanol in a volume ratio of 1:5. The methanol was decanted off, and the precipitated polymer was washed three times with fresh methanol (1:5 volume ratio) to give a rubbery granular product.

TABLE

	Example 9	Example 10	Example 11
diol:diisocyanate molar ratio	1:0	2:1	3:2
Mn	11440	12340	13240
Mw	134800	142000	122600
Mw/Mn	11.78	11.51	9.26
E ^{1.0}	520	669	823
ϵ_m (%)	311	897	536
ϵ_f (failure) (%)	372	1082	562
σ_m (psi)	153	345	300
σ_m (corrected) (psi)	678	3575	2381
ShoreA	49	60	65

The foregoing detailed description of the preferred embodiments of the invention has been provided for the purpose of explaining the principles of the invention and its practical application, thereby enabling others skilled in the art to understand the invention for various embodiments and with various modifications as are suited to the particular use contemplated. The foregoing detailed description is not intended to be exhaustive or to limit the invention to the precise embodiments disclosed. Modifications and equivalents will be apparent to practitioners skilled in this art and are encompassed within the spirit and scope of the appended claims.

WHAT IS CLAIMED IS:

1. A method of preparing a thermoplastic elastomer having A blocks which are crystalline at temperatures below about 75°C and the B blocks which are amorphous at temperatures above about -20°C, the method comprising:

5 (a) dissolving the A blocks and B blocks terminated with respective isocyanate-reactive groups at approximately the stoichiometric ratios that are intended to be present in the thermoplastic elastomer into solution comprising at least one non-halogenated solvent, the A blocks being crystalline at temperatures below about 75°C and derived from monomers comprising at least one member selected from the group
10 consisting of oxetane derivatives and tetrahydrofuran derivatives, the B blocks being amorphous at temperatures above about -20°C and derived from monomers comprising at least one member selected from the group consisting of oxetane and derivatives thereof, tetrahydrofuran and derivatives thereof, and oxirane and derivatives thereof;

15 (b) drying the dissolved A blocks and B blocks of water by azeotropic distillation of the non-halogenated solvent;

(c) end-capping the dried A blocks and the dried B blocks in the non-halogenated solvent by reacting the dried A blocks and the dried B blocks with at least one diisocyanate in which a first isocyanate moiety thereof is substantially more
20 reactive with the terminal groups of the blocks as a second isocyanate moiety thereof, whereby the more reactive first isocyanate moiety is capable of reacting with the terminal groups of the blocks, leaving the less reactive second isocyanate moiety free and unreacted; and

(d) linking the end-capped A blocks and the end-capped B blocks together
25 in the non-halogenated solvent with at least one linking compound comprising two isocyanate-reactive groups which are sufficiently sterically unhindered to react with the free and unreacted isocyanate moieties of the end-capped polymers.

2. A method as defined in claim 1, wherein said dissolving step (a) comprises separately dissolving the A blocks and the B blocks into respective solutions.

3. A method as defined in claim 2, wherein said end-capping step (c) comprises separately end-capping the A blocks and the B blocks in the respective solutions.

4. A method as defined in claim 1, wherein said steps (a), (b), (c), and (d) are conducted in the absence of any halogenated solvent.

5. A method as defined in claim 1, wherein the non-halogenated solvent comprises one or more organic ethers.

6. A method as defined in claim 5, wherein the organic ether comprises one or more members selected from the group consisting of tetrahydrofuran, ethylene glycol dimethyl ether, and 1,4-dioxane.

7. A method as defined in claim 6, wherein the organic ether comprises tetrahydrofuran.

8. A method as defined in claim 1, wherein the non-halogenated solvent comprises one or more organic esters.

9. A method as defined in claim 8, wherein the organic ester comprises ethyl acetate.

10. A method as defined in claim 1, wherein the non-halogenated solvent comprises one or more organic ketones.

11. A method as defined in claim 10, wherein the organic ketone comprises methyl ethyl ketone.

12. A method as defined in claim 1, wherein the linking compound is derived from at least one diisocyanate and at least one difunctional urethane oligomer comprising two functional groups which are reactive with isocyanate moieties of the diisocyanate.

5 13. A method as defined in claim 1, wherein:

the first isocyanate moiety of the diisocyanate is at least five times more reactive with the terminal groups of each of the blocks as the second isocyanate moiety, whereby the more reactive first isocyanate moiety is capable of reacting with and end capping the terminal groups of the blocks, leaving the less reactive second
10 isocyanate moiety free and unreacted; and

the linking compound has two isocyanate-reactive hydroxyl groups which are sufficiently sterically unhindered to be reactive with the free and unreacted second isocyanate groups of the end-capped blocks.

14. A method as defined in claim 1, wherein the diisocyanate comprises
15 toluene diisocyanate.

15. A method as defined in claim 1, wherein the thermoplastic elastomer has a weight average molecular weight of at least 40,000 and a number average molecular weight of at least 10,000.

16. A method as defined in claim 1, wherein the thermoplastic elastomer
20 has a weight average molecular weight of at least 60,000 and a number average molecular weight of at least 12,000.

17. A method as defined in claim 1, wherein the thermoplastic elastomer has a weight average molecular weight of at least 80,000 and a number average molecular weight of at least 15,000.

18. A method as defined in claim 1, wherein the isocyanate-reactive terminal groups of the A and B blocks are hydroxyl groups.

19. A method of making an energetic composite binder comprising:

5 (a) dissolving the A blocks and B blocks terminated with respective isocyanate-reactive groups at approximately the stoichiometric ratios that are intended to be present in the thermoplastic elastomer into solution comprising at least one non-halogenated solvent, the A blocks being crystalline at temperatures below about 75°C and derived from monomers comprising at least one member selected from the group consisting of oxetane derivatives and tetrahydrofuran derivatives, the B blocks being
10 amorphous at temperatures above about -20°C and derived from monomers comprising at least one member selected from the group consisting of oxetane and derivatives thereof, tetrahydrofuran and derivatives thereof, and oxirane and derivatives thereof;

(b) drying the dissolved A blocks and B blocks of water by azeotropic
15 distillation of the non-halogenated solvent;

(c) end-capping the dried A blocks and the dried B blocks in the non-halogenated solvent by reacting the dried A blocks and the dried B blocks with at least one diisocyanate in which a first isocyanate moiety thereof is substantially more reactive with the terminal groups of the blocks as a second isocyanate moiety thereof,
20 whereby the more reactive first isocyanate moiety is capable of reacting with the terminal groups of the blocks, leaving the less reactive second isocyanate moiety free and unreacted;

(d) linking the end-capped A blocks and the end-capped B blocks together in the non-halogenated solvent with at least one linking compound comprising two
25 isocyanate-reactive groups which are sufficiently sterically unhindered to react with the free and unreacted isocyanate moieties of the end-capped polymers; and

(e) blending the thermoplastic elastomer with about 50 wt% to about 95

wt% of at least one solid selected from the group consisting of fuel material particulates and oxidizer particulates.

20. A method as defined in claim 19, wherein said dissolving step (a) comprises separately dissolving the A blocks and the B blocks into respective
5 solutions.

21. A method as defined in claim 20, wherein said end-capping step (c) comprises separately end-capping the A blocks and the B blocks in the respective solutions.

22. A method as defined in claim 19, wherein said steps (a), (b), (c), and
10 (d) are conducted in the absence of any halogenated solvent.

23. A method as defined in claim 19, wherein the non-halogenated solvent comprises one or more organic ethers.

24. A method as defined in claim 23, wherein the organic ether comprises one or more members selected from the group consisting of tetrahydrofuran, ethylene glycol dimethyl ether, and 1,4-dioxane.
15

25. A method as defined in claim 23, wherein the organic ether comprises tetrahydrofuran.

26. A method as defined in claim 19, wherein the non-halogenated solvent comprises one or more organic esters.

20 27. A method as defined in claim 26, wherein the organic ester comprises ethyl acetate.

28. A method as defined in claim 19, wherein the non-halogenated solvent comprises one or more organic ketones.

29. A method as defined in claim 28, wherein the organic ketone comprises methyl ethyl ketone.

30. A method of making a rocket motor propellant comprising making a binder as defined in claim 19.

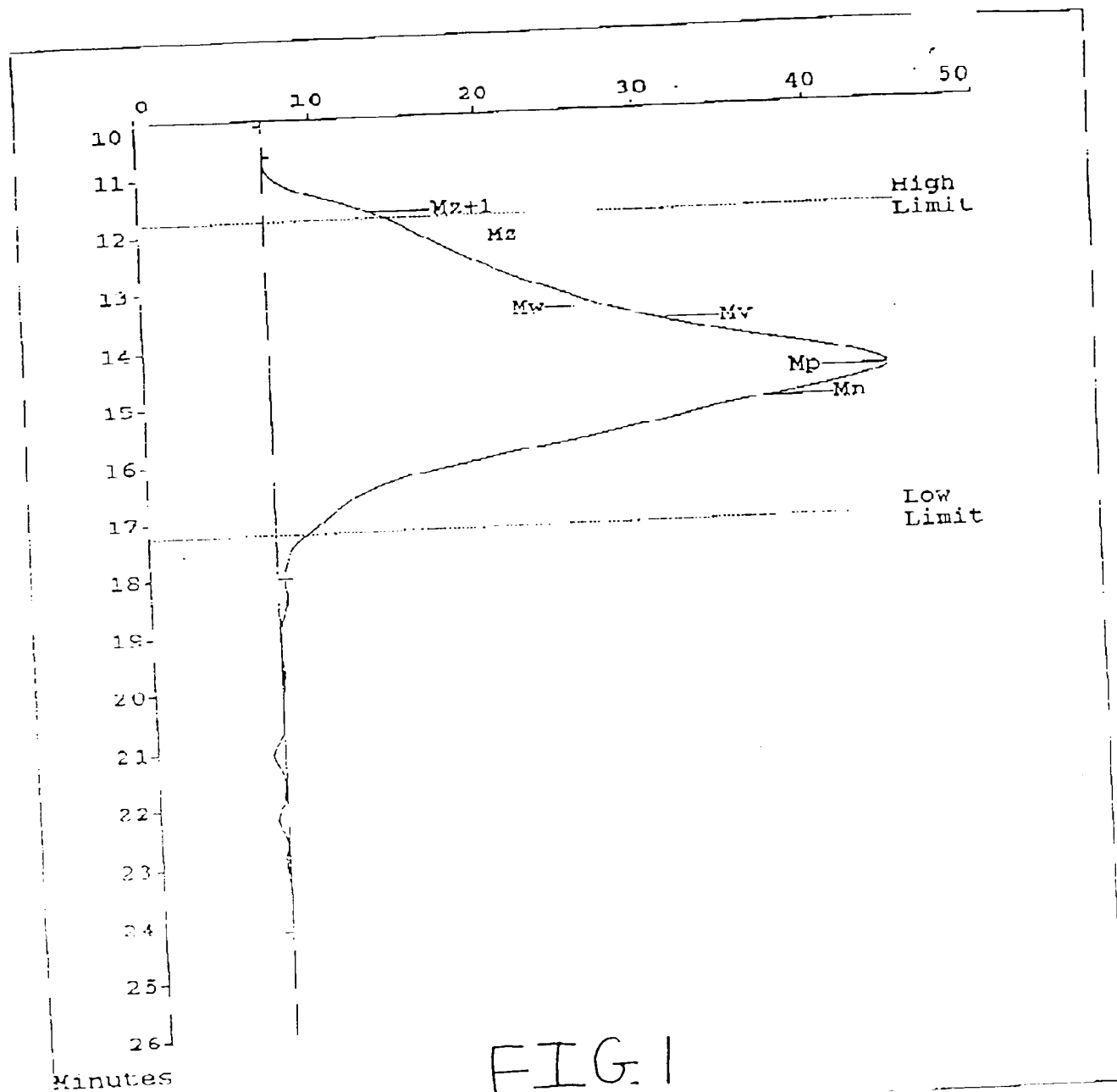
5 31. A method of making a gun propellant comprising making a binder as defined in claim 19.

32. A method of making an explosive comprising making a binder as defined in claim 19.

10 33. A method of making a gasifier comprising making a binder as defined in claim 19.

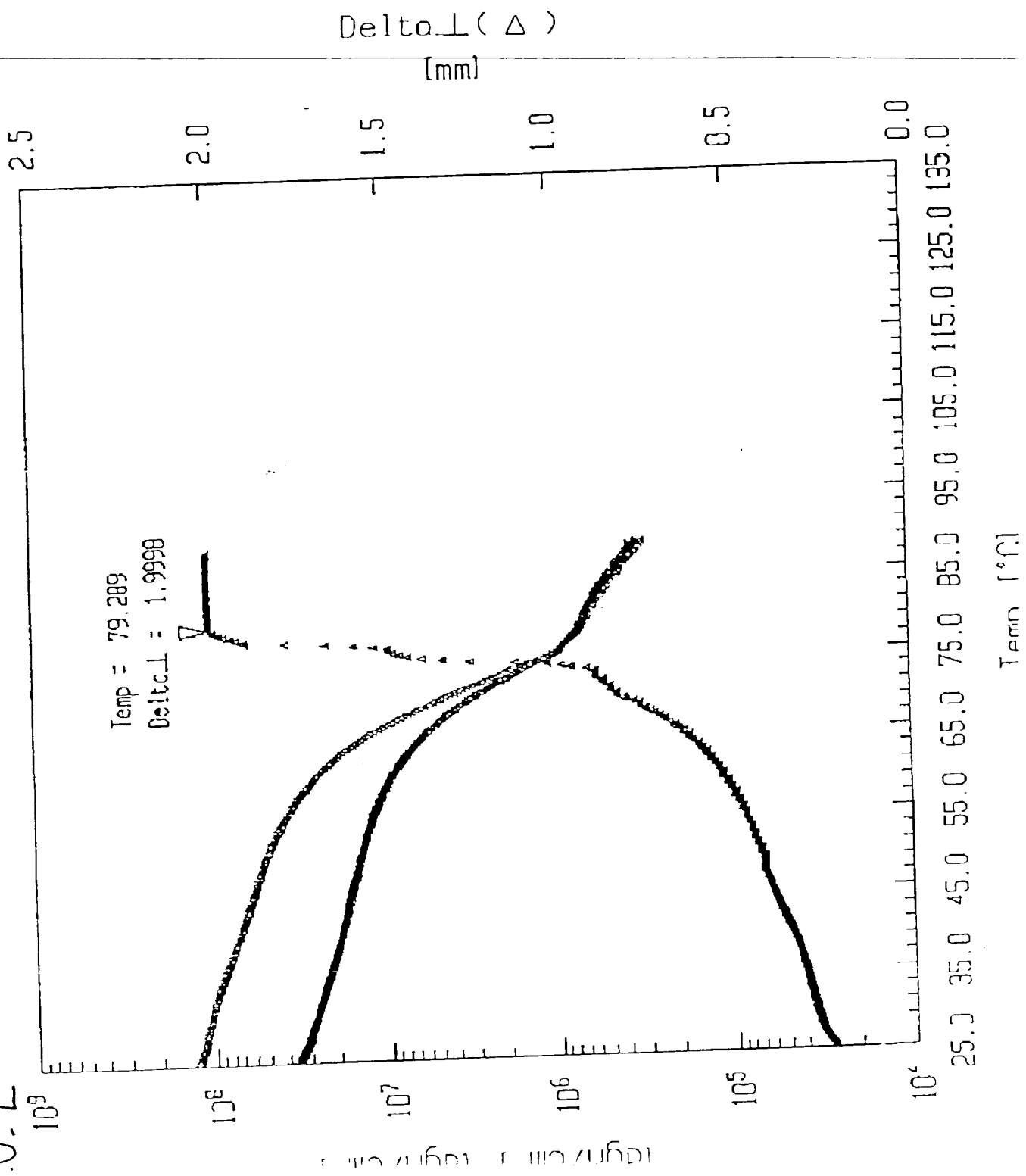
ABSTRACT OF THE DISCLOSURE

A method of preparing a thermoplastic elastomer having A blocks which are crystalline at temperatures below about 75°C and B blocks which are amorphous at temperatures above about -20°C is disclosed. The A blocks are derived from oxetane derivatives and/or tetrahydrofuran derivatives. The B blocks are derived from oxetanes, tetrahydrofuran, oxiranes, and derivatives thereof. The A blocks and B blocks are dissolved into solution containing a non-halogenated solvent, preferably tetrahydrofuran. The dissolved A blocks and B blocks are dried of water by azeotropic distillation of the non-halogenated solvent. Next, the dried A blocks and the dried B-blocks are end-capped with a diisocyanate having one isocyanate moiety substantially more reactive with the terminal groups of the blocks than the other isocyanate moiety, whereby the more reactive isocyanate moiety is capable of reacting with the terminal groups of the blocks, leaving the less reactive isocyanate moiety free and unreacted. The end-capped A blocks and the end-capped B blocks are linked together with a linking compound having two isocyanate-reactive groups which are sufficiently unhindered to react with the free and unreacted isocyanate moieties of the end-capped polymers.



G.2

25% BAMO-GAP : 1561/51 4/15/98



From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

COLTON, Kendrew H.
PILLSBURY MADISON & SUTRO, LLP
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ETATS-UNIS D'AMERIQUE

PCT

NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL PRELIMINARY
EXAMINATION REPORT

(PCT Rule 71.1)

Date of mailing
(day/month/year)

02.02.01

Applicant's or agent's file reference
98-33-SE PCT

IMPORTANT NOTIFICATION

International application No.
PCT/US99/24013

International filing date (day/month/year)
09/11/1999

Priority date (day/month/year)
12/11/1998

Applicant
CORDANT TECHNOLOGIES, INC. et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.



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PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 98-33-SE PCT	FOR FURTHER ACTION		See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/US99/24013	International filing date (<i>day/month/year</i>) 09/11/1999	Priority date (<i>day/month/year</i>) 12/11/1998	
International Patent Classification (IPC) or national classification and IPC C08G18/08			
Applicant CORDANT TECHNOLOGIES, INC. et al.			

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 7 sheets, including this cover sheet.

☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

 These annexes consist of a total of 3 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☒ Certain defects in the international application
- VIII ☒ Certain observations on the international application

09/06/2000

0 2. 02. 01

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**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/US99/24010

I. Basis of the report

1. This report has been drawn on the basis of *(substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments (Rules 70.16 and 70.17).):*

Description, pages:

3-8,10-27 as originally filed

1,2,9 as received on 09/06/2000 with letter of 09/06/2000

Claims, No.:

1-33 as originally filed

Drawings, sheets:

1/2,2/2 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
☐ the language of publication of the international application (under Rule 48.3(b)).
☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
☐ filed together with the international application in computer readable form.
☐ furnished subsequently to this Authority in written form.
☐ furnished subsequently to this Authority in computer readable form.

When a sequence listing has been furnished, the international preliminary examination was carried out on the basis of the sequence listing as furnished, unless the Authority has indicated otherwise.

4. The amendments have resulted in the cancellation of:

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/US99/24013

- ☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

5. ☒ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

see separate sheet

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-33
	No:	Claims	
Inventive step (IS)	Yes:	Claims	5-12 and 23-29
	No:	Claims	1-4, 13-22, 30-33
Industrial applicability (IA)	Yes:	Claims	1-33
	No:	Claims	

2. Citations and explanations

see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/US99/24013

Re Item I

Basis of the opinion

The amendments filed with the letter dated 09. 06. 2000 introduce subject-matter which extends beyond the content of the application as filed, contrary to Article 34(2)(b) PCT. The amendments concerned are the following:

The replacement of the first formula on page 9 by another one.

Both the original and the amended formula depict THF derivatives. Even if the expert might regard the original formula as being wrong, it was not immediately evident that the original formula was to be replaced by the one on amended page 9. One could also think of a formula where at least one of the radicals R_1 , R_2 , R_3 or R_4 is situated at a carbon atom adjacent to the oxygen of the tetrahydrofuran ring. It should be borne in mind that no specific THF derivatives are disclosed in the present application.

Re Item V

Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Cited literature

(a) Reference is made to the following documents:

D1: US-A-4 806 613

D2: US-A-5 210 153

D3: US-A-4 393 199

(c) Document **D3** which is cited at 4.22-26 of the present description was not mentioned in the international search report. A copy of the document was appended to the written opinion.

2. Novelty

Document **D1** is considered to represent the most relevant prior art. It describes a process (see claim 1 and examples 9 and 10) which differs from the one of the present claims in that no non-halogenated solvent is employed. In the examples CH_2Cl_2 is used as the solvent. At 8/60-62 no specific solvent is mentioned.

For this reason, the subject-matter of the present claims is novel.

3. Inventive step

- (a) The problem solved by using a non-halogenated solvent was to avoid the use of solvents that have a detrimental effect on the environment (see 4/2-3).
- (b) The use of a non-halogenated solvent for this purpose was obvious in view of **D2**, example 9. Said example mentions that benzene, dichloromethane or tetrachloroethane are useful as solvents for the soft block (e.g. BMMO/THF). In contrast to the applicant's view there is no indication in this example that dichloromethane or tetrachloroethane should be used *in lieu of* benzene. The expert thus knew that he could replace the dichloromethane employed in **D1** by benzene and thereby avoid a solvent hazardous to the ozone layer of the earth.
- (c) For this reason, the subject-matter of claims 1-4, 13-22 and 30-33 is not deemed to be based on an inventive step.
- (d) None of the cited documents does, however, suggest to use organic ethers, esters or ketones as solvents.

- that document **D3** mentions the use of a rather exotic solvent, i.e. a rather exotic solvent (see **D3**, 10/5-15), i.e. a rather exotic solvent, and

- that halogenated solvents were used throughout the examples of the cited documents, and that example 9 of **D2** mentions the use of a halogenated solvent.

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/US99/24013

it is not deemed to be obvious to the expert to replace the solvents employed in the prior art by organic ethers, esters or ketones.

- (e) Nor is there any suggestion to use a linking component derived from at least one diisocyanate and at least one difunctional urethane oligomer (see present claim 12).
- (f) Consequently the subject-matter of **claims 5-12 and 23-29** is deemed to be inventive.

Re Item VII

Certain defects in the international application

1. The terms "the complete disclosures of which are incorporated ... with this invention" and the like at 3/7-9, 13/3-18 and 19/8-9) leave doubt as to the actual disclosure of the present invention. Said terms should have been deleted.
2. The word "about" should have been deleted in the description whenever relating to ranges mentioned in the present claims (see 5/11-12, 7/3-5+10 and 10/11-14).
3. The reference to the application number at 13/16-17 should have been deleted or replaced by one to the respective publication or patent number.
4. The word "Preferably" should have been deleted at 14/5+16 (see claim 1).
5. The sentence at 14/28-15/2 should have been deleted as the NCO-groups in the

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/US99/24013

Re Item VIII

Certain observations on the international application

Clarity of the claims

- (a) The word "about" blurs the ranges given in **claims 1 and 19** (cf. 28/3+4+8+11 and 31/7+10+27) thus rendering these claims unclear.
- (b) The statement in the description at 27/12-15 implies that the subject-matter for which protection is sought may be different to that defined by the claims, thereby resulting in lack of clarity (Article 6 PCT) when used to interpret them (see also the PCT Guidelines, III-4.3a).
- (c) There is a discrepancy between **claims 1 and 19** (see 28/8 and 31/7: "below about 75 °C") and the description at 5/11 ("below about 60 °C) and at 7/3-4+10.

METHOD FOR THE SYNTHESIS OF ENERGETIC THERMOPLASTIC ELASTOMERS IN NON-HALOGENATED SOLVENTS

Priority is claimed on U.S. provisional application 60/108,455 filed on November 12, 1998

BACKGROUND OF THE INVENTION

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1. Field of the Invention

This invention relates to a method of synthesizing energetic thermoplastic elastomers which are useful as binders of high energy compositions, such as rocket motor propellants, gun propellants, explosive munitions, gas generants of vehicle supplemental restraint systems, or the like.

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2. Description of the Related Art

Solid high energy compositions, such as propellants, explosives, gas generants, and the like comprise solid particulates, such as fuel particulates and/or oxidizer particulates, dispersed and immobilized throughout a polymeric binder matrix.

15

Conventional solid composite propellant binders utilize cross-linked elastomers in which prepolymers are cross-linked by chemical curing agents. As outlined in detail in U.S. Patent No. 4,361,526, there are important disadvantages to using cross-linked elastomers as binders. Cross-linked elastomers must be cast within a short period of time after addition of the curative, which time period is known as the "pot life". Disposal of a cast, cross-linked propellant composition is difficult, and usually is accomplished by burning, which poses environmental problems. Furthermore, current state-of-the-art propellant compositions have serious problems that include their use of nonenergetic binders which have lower performance and high end-of-mix viscosities.

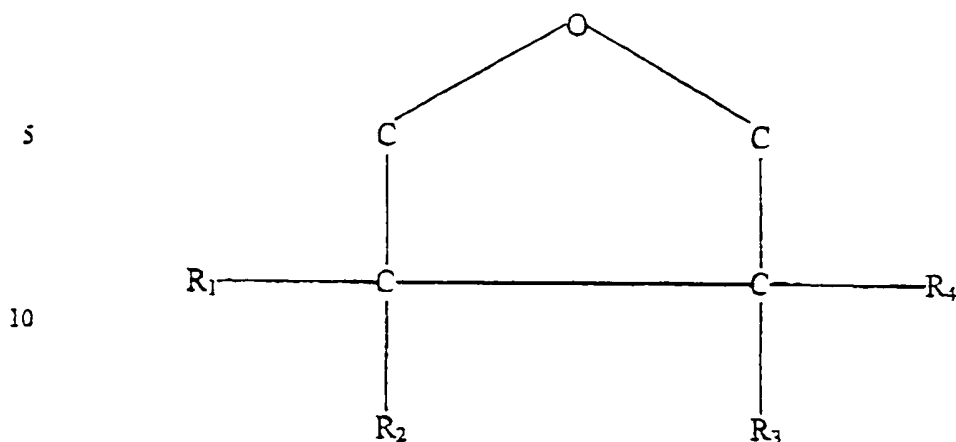
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In view of the inherent disadvantages associated with the use of cross-linked elastomeric polymers as binder materials, there has been considerable interest in finding new, non-cross-linked thermoplastic elastomers that meet important requirements expected of propellant formulations, particularly the requirement of

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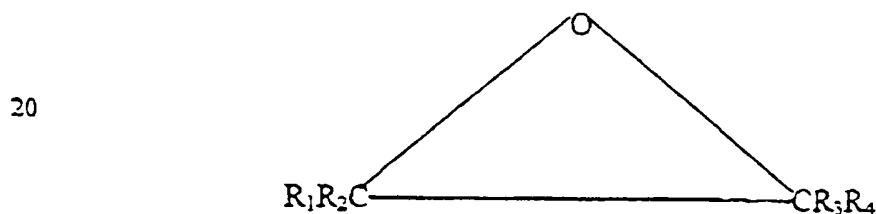
SUBSTITUTE SHEET

AMENDED SHEET



15 wherein the R₁-R₄ groups are the same or different and are selected from moieties set forth above in connection with the description of suitable oxetane derivatives.

Oxirane monomer units used in forming the B blocks of the present invention have the general formula:



wherein R₁ and R₃ are independently selected from hydrogen and methyl, and R₂ and R₄ are independently selected from hydrogen, alkyl containing from 1 to 10 carbon atoms, chloroalkyl and bromoalkyl containing 1 to 2 carbon atoms, and nitroalkyl, nitroalkoxyalkyl, nitroalkyl, nitroalkoxyalkyl, azidoalkyl, azidoalkoxyalkyl,

25